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ANNULÉ



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OSMOTIC PRESSURES OF CONCENTRATED SOLUTIONS

BY WILDER D. BANCROFT AND HERBERT L. DAVIS

Introduction

Probably the largest single contribution to the theory of solutions was made by van't Hoff in his papers,¹ in which he elaborated the analogy between osmotic pressure and gas pressure. Many articles have since appeared as extensions of or deductions from the generalizations there enunciated; but it seems that the most fundamental relation, that between osmotic pressure and the vapor pressure of a solution, was not stated very clearly by van't Hoff nor understood thoroughly by those who have worked on such problems since. Several authors have indeed given fairly complete and accurate statements of the van't Hoff equations; but so many more have erred in applying them or their simplifications and extensions to actual data that it appears desirable to derive the equations again, and to point out some useful applications of them.

It may be made clear that this paper will not deal with the vexed question of just what the nature of osmotic pressure is, nor to what it is due. Those interested may find a very interesting discussion of that in the Transactions of the Faraday Society for June, 1918 vol. 13, pp. 119-189. For our purpose, it will be sufficient to follow van't Hoff.²

"In order clearly to realize the quantity referred to as osmotic pressure, imagine a vessel, A, completely full of an aqueous solution of sugar, placed in water B. If it be conceived that the solid walls of this vessel are permeable to water but impermeable to the dissolved sugar, then, owing to the attraction of the solution for water, water will enter the vessel A up to a certain limit, thereby increasing the pressure on the walls of the vessel. Equilibrium then ensues, owing to the pressure resisting further entry of water. This pressure we have termed *osmotic pressure*."

There are two forms of the equation connecting osmotic pressure and vapor pressures that may be deduced by the aid of the reversible cycle of transformations so useful to van't Hoff. Certain assumptions which will be introduced into the derivation will be stated as need for them arises. Subject to these well-recognized and easily evaluated limitations, the equations derived are absolutely accurate and general.

Derivation of Form I.

We may imagine the solution in a cylinder fitted with a piston permeable to the solvent but not to the solute. The system is at constant temperature.

i. The piston is pushed in far enough to squeeze out one gram of solvent from so large a volume of solution that the concentration change produced

¹ Z. physik. Chem., 1, 481 (1887); Kongl. svenska Vetenskaps Akademiens Handlingar, 21, 3 (1885); Phil. Mag., (5) 26, 81 (1888).

² Phil. Mag., (5) 26, 81 (1888).

shall be negligible. By taking a sufficiently large amount of the solution, ten million liters for example, the error introduced by this, the first assumption, can be made as small as one pleases. In pressing out this gram of solvent, the piston must move through V_s , the volume of one gram of the solvent *in the solution* and against the osmotic pressure P of the solution. The work done then will be:

$$W_1 = PV_s$$

work done on the system being called positive.

2. This gram of solvent may then be vaporized at its own vapor pressure. The second assumption here introduced is that the volume of solvent as liquid is negligible in comparison with its volume as vapor at the same temperature. At ordinary temperatures, one can usually ignore the error here introduced which is of the order of one part in four thousand for water at 25°C ; but which becomes very large as one approaches the critical temperature. In accordance with this, then

$$W_2 = -\frac{p_0 v_0}{M_2}$$

where p_0 and v_0 are the vapor pressure of the pure solvent and its mol volume at that pressure, and M_2 is the molecular weight of the solvent in the *vapor* and not the liquid.

3. The gram of solvent vapor is then permitted to expand from the vapor pressure of the pure solvent (p_0) to the vapor pressure of the solution p_1 . Here is introduced the third and last assumption,—that the vapor of the solvent follows the gas laws. This introduces very little error for most solvents although, of course, acetic acid is barred, because its molecular weight in the vapor is a function of the pressure. If $pv = RT$, we get by differentiating $vdp + pdv = 0$ and $vdp = -pdv$. Also $v = RT/p$, whence $vdp = RT dp/p$. The work done in this step will be

$$\begin{aligned} W_3 &= -\frac{1}{M_2} \int_{v_0}^{v_1} pdv \\ &= +\frac{1}{M_2} \int_{p_0}^{p_1} vdp = -\frac{1}{M_2} \int_{p_1}^{p_0} RT \frac{dp}{p} \\ &= -\frac{RT}{M_2} \ln \frac{p_0}{p_1} \end{aligned}$$

In this derivation v_1 is the volume of one mol of solvent vapor under pressure p_1 , the vapor pressure of the solution.

4. The gram of solvent vapor at pressure p_1 and occupying volume v_1 is condensed reversibly into the solution and the work done is

$$W_4 = \frac{p_1 v_1}{M_2}$$

According to the second law of thermodynamics, the resultant work produced by such a reversible, isothermal, cycle must be zero.

$$W_1 + W_2 + W_3 + W_4 = 0$$

or
$$PV_s - \frac{p_0 v_0}{M_2} - \frac{RT}{M_2} \ln \frac{p_0}{p_1} + \frac{p_1 v_1}{M_2} = 0;$$

and since $p_0V_0 = p_1V_1$

$$PV_s = \frac{RT}{M_s} \ln \frac{p_0}{p_1}, \quad (I)$$

which may be written

$$PV_m = RT \ln \frac{p_0}{p_1}, \quad (I)$$

in which V_m is the volume of one gram of solvent in the solution multiplied by the molecular weight of the solvent in the vapor, P is the osmotic pressure, p_0 and p_1 are the vapor pressures of the pure solvent and the solution respectively, R is the usual gas constant, and T , the absolute temperature. This equation will be referred to hereafter as Form I. V_m is obviously the volume in the solution of a mass of the solvent equal to one gram molecular weight of the solvent in the vapor state.

Van't Hoff¹ early arrived at this relation in discussing the measurements of chemical affinity as applied for concreteness to some salt hydrates whose vapor pressures had been measured. He assumes that in his infinitely dilute solution the density of water is one and derives the formula

$$P = 4.55 T \ln \frac{p_0}{p_1}$$

for the case of water. In this formula,

$$4.55 = \frac{1000 R}{18} = \frac{R}{V_m}$$

where R is the gas constant and V_m is the volume, in liters, in the solution of eighteen grams of water. This is clearly the molecular weight of water as a vapor and not as a liquid. The other terms are defined as they have been previously in this paper.

Using the values of osmotic pressure calculated by this formula, van't Hoff then calculated the work done by this affinity. From the vapor pressure relations the osmotic pressure of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is calculated as 1300 atmospheres. The work done when 18 kilograms of water pass through a semi-permeable membrane into a hypothetical $\text{CuSO}_4 \cdot 4\text{H}_2\text{O}$ is formulated as

$$A = 1300 \times 10333 \times \frac{18}{1000}$$

In this expression, 10333 is the conversion factor of atmospheres to kilograms per square meter, so that 1300×10333 is the P term. Also in the same way as above, $18/1000$ represents the volume of the water introduced, and is the V_m term as used in this paper. Therefore A represents our PV_m term, the work done in the first step of this derivation. Since van't Hoff also shows that

$$A = RT \ln \frac{p_0}{p_1}$$

we have

$$PV_m = RT \ln \frac{p_0}{p_1}$$

¹ "Études de Dynamique chimique," 187 (1884).

Exactly the same derivation is given in Cohen's¹ revision of this earlier book which was translated into English by Ewan.

Van't Hoff² makes practically the same derivation in his equation for the determination of "i" by vapor pressure. He assumes that a one percent sugar solution is sufficiently dilute to render all correction negligible. A translation is substantially as follows:

"The relation is derived from a cycle of reversible transformations at constant temperature in which one first removes 18 kg. of water from a solution (1:100) in the form of vapor which is then compressed to complete condensation to cause it to reenter the solution through a semipermeable wall. The work absorbed during the separation of the water must be equal to that which caused its return to the solution. This work is

$$RT \ln \frac{1}{1 - \Delta}$$

where $1/(1 - \Delta)$ is the ratio between the vapor pressures of the water and the solution."

"The work which accomplishes the return of the water is equal to the product of its volume in cubic meters and the osmotic pressure in kilograms per square meter and equals $\frac{18}{1000 \times s} P$ where s is the density of the water."

Van't Hoff then proceeds to add to this last, other approximations which led to the simplified relation he desired. It is evident that s will be the density of the water in the solution and only for the infinitely dilute solution will it approach the density of the pure solvent. Therefore, in perfectly general terms $1/s = V_s$ and the second work term equals

$$V_s \times 18 \times P$$

or PV_m as defined above. The first work term $RT \ln \frac{1}{1 - \Delta}$ may be written

$RT \ln \frac{p_0}{p_1}$ and these terms equated, as was done above, into:

$$PV_m = RT \ln \frac{p_0}{p_1} \quad (1)$$

Since van't Hoff first published the derivation as given above, several other workers have presented derivations of this formula or of formulas closely similar to it. Gouy and Chaperon³ were the first of these. Their derivation was quite similar to the one here employed except that they introduced the assumption that, for expressing the osmotic pressure exerted between two solutions of slightly differing concentrations, they could neglect the change in density of the water in the process of solution, although they clearly recognized that such a change existed and that the volume to be introduced should be the volume of the *solvent* in the *solution* and not in the pure solvent. They omit the molecular weight of the solvent in the vapor and give the formula as

¹ "Studies in Chemical Dynamics," 236 (1896).

² Kongl. svenska Vetenskaps Akademiens Handlingar, 21, 32 (1885).

³ Ann. Chim. Phys., (6) 13, 120 (1888).

$$P = \pm D_0 RT \ln \frac{p_0}{p_1}$$

where D_0 is the density of the pure solvent. They express the work done in changing unit mass of vapor from p_0 to p_1 as $RT \ln (p_0/p_1)$; but this will be true only if unit mass be a gram molecular weight of the vapor, for this value only is associated with R , the gas constant. This will be clear from step three in the present derivation.

Van Laar¹ derived Form I and also introduced an approximation which will be discussed later, and which was adopted and used by Frazer and Myrick (1916). Ewan² also gives Form I as having been first derived by van't Hoff and then by several other authors.

Porter³ made a very careful deduction similar to the one here presented, but introducing in addition correcting factors for the effect of pressure on the volumes and pressures involved. The exact equation derived by Porter consists of three integrals and is consequently not so immediately useful as the forms here given. He too presses out one gram of solvent and his resultant equation, after certain simplifying assumptions are made, is approximately

$$P_s = RT \ln \frac{p_0}{p_1}$$

in which s is the reduction in volume of solution when one gram of solvent escapes—that is V_g as we have defined it. In this equation also, there is no term for the molecular weight of the solvent.

Callendar⁴ shared in this general development, considering somewhat the question of hydration of the solute. Findlay⁵ reviews the whole problem quite thoroughly, but seems to regard the so-called thermodynamic equation (Form I of the present paper) as not immediately useful or at least useful only for the ideal solutions which will be discussed later. Kendall⁶ gives a most interesting discussion of Form I, calling it "the dilute-solution equation." He seems to exhibit a better comprehension of the equation and its real meaning than most authors who have touched on it. He points out clearly why it is useless for the calculation of solvent association. Mellor⁷ discusses osmotic pressure at length but does not give the form derived here. The nearest approach to it is

$$P + \frac{\alpha P^2}{2} = - \frac{RT}{V_0} \log (1 - N')$$

which will be shown later to involve the assumption of an ideal solution. In this equation α is the compressibility factor of the solvent, N' is the mol fraction of the solute and V_0 is the mol volume of the solvent.

¹ Z. physik. Chem., 15, 457 (1894).

² Z. physik. Chem., 14, 410 (1894).

³ Proc. Roy. Soc., 79A, 521 (1907).

⁴ Proc. Roy. Soc., 80A, 466 (1908).

⁵ "Osmotic Pressure," 55 (1919).

⁶ J. Am. Chem. Soc., 43, 1391 (1921).

⁷ "Treatise on Inorganic and Theoretical Chemistry," 1, 552 (1922).

At various times, Frazer has dealt with the question of osmotic pressure and in a recent chapter¹ presents a derivation similar to the one used here and comes out with

$$P = \frac{RT}{v_0} \ln \frac{p_0}{p_1}$$

in which v_0 is the molal volume of the solvent in the solution, and consequently V_m as used here, provided that the molecular weight used in calculating v_0 be the molecular weight of the solvent as vapor and not in the solution. Frazer does not mention this point although it certainly enters in aqueous solutions, the osmotic pressures of which he has measured so well. However, in most of his work he assumes an ideal solution for which the molecular weight in the vapor must be the same as in the solution. W. C. McC. Lewis² derives Form I using slightly different notation and is quite clear that the molecular weight of the solvent as vapor is to be introduced.

The general expression connecting osmotic pressure and vapor pressure of a solution is then our Form I,

$$PV_m = RT \ln \frac{p_0}{p_1}$$

It will be well to observe that in this expression there is no term for the concentration of the solution, only the vapor pressures of the solvent and solution, the temperatures and the value of V_m being needed for the calculation of the osmotic pressure. Also, as Kendall³ points out, the expression can have no value in indicating the extent of association of the solvent. Attempts have been made in vain to determine by its aid the existence of, or the extent of, association of water in aqueous solution. The molecular weight introduced must be the molecular weight of the solvent in the vapor state and most solvent vapors are not associated regardless of their condition in the liquid state or in the solution. An interesting exception to this is the case of acetic acid as solvent which Raoult and Recoura⁴ found to give quite abnormal vapor pressure lowerings on addition of solutes which in other solvents were normal. Raoult calculated his mol fractions from the molecular weight of the substances in the solution. Consequently he concluded that this abnormal lowering of the vapor pressure indicated that the apparent molecular weight of acetic acid in the solution was about 97 instead of the formula weight, 60. The apparent abnormality was explained by van't Hoff, who, in a note to the Raoult and Recoura paper, showed again that the molecular weight of the solvent *in the vapor phase* should have been introduced into the calculations. The molecular weight of acetic acid vapor was known to be about 97 and when this value was used instead of 60, acetic acid was found to follow the same law of vapor pressure lowering as did the other solvents. This question will be discussed more at length later in the paper.

¹ Taylor: "Treatise on Physical Chemistry," 275 (1924).

² "A System of Physical Chemistry," 2, 129 (1925).

³ J. Am. Chem. Soc., 43, 1391 (1921).

⁴ Z. physik. Chem., 5, 426 (1890).

Derivation of Form II

There is another form of the osmotic pressure vapor pressure relation which may be derived as was the first, and which involves the same assumptions.

1. In this derivation, the semipermeable piston is pushed in far enough to squeeze out from the solution the number of grams of solvent in which one molecular weight of the solute is dissolved. The work done is

$$W_1 = PV_1,$$

in which P is the osmotic pressure and V_1 is the volume in the solution of that mass of the solvent in which one molecular weight of the solute is dissolved.

2. If the original solution contained g_1 grams of solute to g_2 grams of the solvent, there will be $\frac{g_2 M_1}{g_1}$ grams of the solvent squeezed out or $\frac{g_2 M_1}{g_1 M_2}$ mols of solvent squeezed out, where M_1 is the molecular weight of the solute in the solution and M_2 is the molecular weight of the solvent in the vapor. The work done in evaporating this mass of solvent at its own vapor pressure will be

$$W_2 = - \frac{g_2 M_1}{g_1 M_2} p_0 v_0,$$

where p_0 is the vapor pressure of the pure solvent and v_0 is the volume of one mol of solvent vapor under a pressure of p_0 .

3. This solvent vapor at p_0 is expanded to p_1 , the vapor pressure of the solution, and, by the same processes as were employed in the first derivation, the work term is

$$W_3 = - \frac{g_2 M_1}{g_1 M_2} RT \ln \frac{p_0}{p_1}.$$

4. Condensing the vapor, at pressure p_1 and corresponding v_1 , into the solution gives

$$W_4 = \frac{g_2 M_1}{g_1 M_2} p_1 v_1.$$

As before, the sum of the work terms must equal zero.

$$PV_1 - \frac{g_2 M_1}{g_1 M_2} p_0 v_0 - \frac{g_2 M_1}{g_1 M_2} RT \ln \frac{p_0}{p_1} + \frac{g_2 M_1}{g_1 M_2} p_1 v_1 = 0,$$

from which

$$PV_1 = \frac{g_2 M_1}{g_1 M_2} RT \ln \frac{p_0}{p_1}.$$

Since $\frac{g_1}{M_1} = n$, the number of mols of solute in the solution, and $\frac{g_2}{M_2} = N$, the number of mols the solvent would produce if converted into vapor, we may write

$$PV_1 = \frac{N}{n} RT \ln \frac{p_0}{p_1} \quad (\text{II})$$

This equation will here after be referred to as Form II.

This relation is also to be found in van't Hoff's¹ paper when he derived the relation between concentration and vapor pressure lowering for a very dilute π percent sugar solution substantially as follows:

1. Remove, by the use of a cylinder with semipermeable wall, a portion of the solvent containing a kilogram-molecule (M_1) of the dissolved substance; here the total quantity of solution is supposed to be so great that no alteration of concentration occurs, and the expenditure of work is therefore RT .

2. This quantity, $\frac{100M_1}{\pi}$ kilograms, of the solvent is returned as vapor;

it may be conceived as produced from the liquid by evaporation at its vapor pressure; then expanded until its pressure is equal to the vapor pressure of the solution; and finally liquefied in contact with the solution. The kilogram-molecule of the solvent will thus receive an expenditure of work of $RT\Delta$,

where Δ represents the relative diminution of pressure; and the $\frac{100M_1}{\pi}$ kilo-

grams will receive $RT\Delta \frac{100M_1}{\pi M_2}$. Here $\frac{\Delta M_1}{\pi}$ is Raoult's molecular diminution

of pressure, which we shall term K ; employing this abbreviation, the ex-

pression becomes $\frac{100RTK}{M_2}$.

In a note to the Raoult and Recoura paper in 1890 van't Hoff extended this derivation and made it completely accurate. "In the change of vapor pressure from p_0 to p_1 , if normal densities exist, there is an energy increase

of $RT \ln \frac{p_0}{p_1}$, which for dilute solutions where p_1 differs little from p_0 , becomes

$RT \frac{p_0 - p_1}{p_0}$."

This ratio, $\frac{p_0 - p_1}{p_0}$, is the relative vapor pressure lowering which he previously represented by Δ , and which now is accurately stated should be

$\ln \frac{p_0}{p_1}$. We may now combine the first step of the earlier paper with the corrected value of the second work term in the later paper.

$$PV_1 = RT \Delta \frac{100M_1}{\pi M_2}$$

In this equation $100 = g_2$, $\pi = g_1$ and Δ should be replaced by $\ln \frac{p_0}{p_1}$. Mak-

ing these substitutions and omitting the simplifying approximations van't Hoff introduced, we arrive at the relation previously derived as Form II,

$$PV_1 = RT \frac{N}{n} \ln \frac{p_0}{p_1} \quad (II)$$

¹ Z. physik, Chem., 1, 494 (1887); Phil. Mag., (5) 26, 93 (1888).

The relation between the two forms here derived for the same solution may be shown as follows

$$PV_m = RT \ln \frac{p_0}{p_1} \quad (I)$$

$$PV_1 = RT \frac{N}{n} \ln \frac{p_0}{p_1} \quad (II)$$

Dividing, $V_m/V_1 = n/N$ or in general $nV_1 = NV_m$ which in words merely says that the volume, V_1 , of the solvent in a solution for which $n = 1$ is equal to the mols of solvent present multiplied by the mol volume of the solvent in the solution, the mols present and mol volume of the solvent being calculated on the basis of its molecular weight in the vapor. Since this is, of course, obvious, the equivalence of the two forms is established.

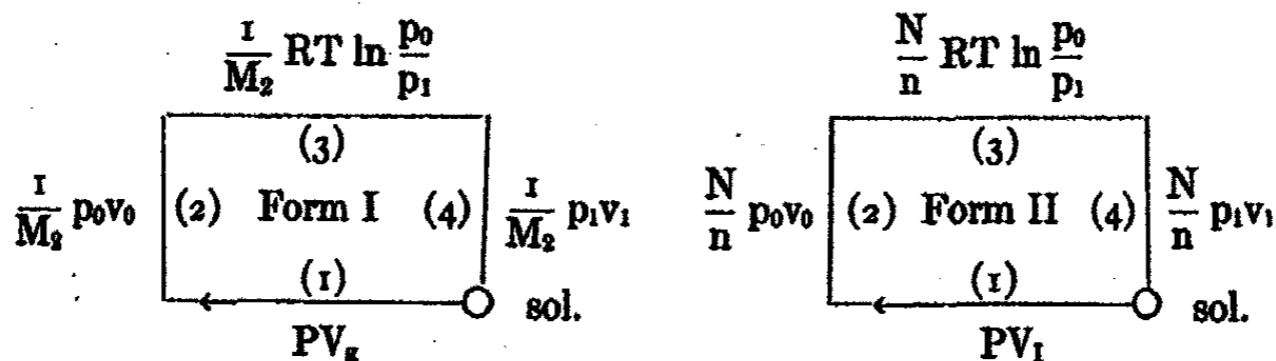
Although Form II appears more useful than Form I, very little work has been done with it. Bancroft¹ gave Form II as having been derived from van't Hoff and went on to show that, if there is an evolution of heat on dilution, the osmotic pressure of the solutions would be larger than that called for by the formula and similarly the lowering of the freezing point of such a solution will be greater than when the heat of dilution is zero.

Before leaving the derivations, it might be well to point out that these equations are perfectly general and are accurate except for the assumptions definitely stated and easily evaluated. Up to the third work term in each equation, the only assumption introduced is that the volume of the solvent as a liquid may be neglected in comparison with its volume as a vapor. This assumption involves only a small, readily calculated, error, and, if it is desired, we may from step three take:

$$PV_g = \frac{1}{M_2} \int_{v_0}^{v_1} p dv$$

which involves only this single assumption and is free from the assumption that the vapor of the solvent follows the gas laws. This form is therefore more accurate than Form I as above derived, but is not so useful.

Possibly the work done in the four steps employed in the above derivations may be represented by a parallelogram such as is here shown:



In the derivation of Form I, one gram of solvent is pressed out of the solution and then returned to it; in Form II, that mass of the solvent in which one mol of solute is dissolved is put through the same cycle. This cycle con-

¹ J. Phys. Chem., 10, 322 (1906).

sists of the four steps as shown: first, pressing it out of the solution; second, vaporizing the solvent at its vapor pressure as a pure liquid; third, permitting it to expand to the vapor pressure of the solution; and finally, condensing it back into the solution. It may be mentioned that the V_1 of Form II contains N/n mols of the solvent, the N always being calculated from the molecular weight of the solvent in the vapor state. In both cases, work terms 2 and 4 are equal and opposite and therefore, the work done in step 1 equals that done in step 3. The cycle is represented by a rectangle for convenience but any parallelogram would serve equally well.

The Use of $PV = RT$ to express Osmotic Pressures

For most chemists, the most interesting item in the original papers of van't Hoff embodying the essentials of the above derivations was not the derivations but was the analogy which he showed to exist between osmotic pressure and gas pressure. This analogy was expressed as follows:¹

"The well-known formula expressing both Boyle's and Gay-Lussac's laws for gases

$$P V = R T$$

are, in so far as these laws are applicable to liquids also applicable as regards osmotic pressure; with the reservation also made in the case of gases, that the space occupied by the molecules must be so great that the actual volume of the molecules becomes negligible."

This limitation however was supplementary to an earlier one stated fully by van't Hoff and discussed at length by Ewan.²

"In 1885 van't Hoff showed that the equation

$$P V = R T$$

which expressed the relation between pressures, temperatures, and volume of a perfect gas, is likewise applicable to the osmotic pressure of a solution. Nevertheless, the behavior of most solutions is not strictly in accord with this equation and the present paper considers certain factors which are not represented in the simple equation $PV = RT$ and thus produces a formulation which is nearer the truth.

"The most important of these factors is, as van't Hoff observed, the heat of dilution of the solution. He says,³ after he has shown that the equation $PV = RT$ is as valid for solutions as for gases; 'Here the same reservations apply as in the case of gases, and the analogy between the two states of matter is such that the reason for the limitation is exactly the same in the two cases. We know that in the case of gases, deviations appear as soon as the concentration of the gas is such that the mutual attraction of the molecules is no longer negligible. By the same reasoning, the laws deduced for solutions can no longer be accepted in such circumstances. We may add that, in the

¹ Phil. Mag., (5) 26, 90 (1888).

² Z. physik Chem., 14, 409 (1894).

³ Kongl. svenska Vetenskaps Akademiens Handlingar, 21, 12 (1885).

case of solutions, this mutual effect of the solute particles on each other is easily observed; during the process of dilution, this effect gives rise to the production of internal work terms which are manifested in their thermal equivalents. Consequently the laws here derived apply to those solutions so dilute that the heat of dilution becomes negligible."

Ewan then continues:

"By taking into account heat of dilution and the volume changes that appear on dilution, I have obtained certain equations for the relation between osmotic pressure, temperature, volume and heat of dilution which are so constructed that, when the heat of dilution and the volume changes are zero, the equations become identical with those derived by van't Hoff."

By means of equations then developed, Ewan was able to calculate the vapor pressures of some sulphuric acid solutions from the freezing points and heats of dilution. Ewan dealt with the quantitative conversion of the heat of dilution into work at the changing temperatures of the freezing points. Neither he nor anyone else has yet evaluated the heat of dilution at constant temperature as a work term. Until this is done, no simple equation of the form, $P V = R T$ plus or minus some work term, can be derived for the calculation of osmotic pressures. The equations here developed as Forms I and II are perfectly general and need no further correcting factors of any sort to express osmotic pressures.

Since these factors were difficult to evaluate and of less real interest than the fundamental relation, much of the subsequent theoretical development has been along the line of the ideal solution and this will be discussed at this point in order to make clear some references that have preceded this and many that follow. The concept of ideal solutions was introduced to obviate the necessity of introducing the heat of dilution.

Ewan¹ himself, five years after the above paper was published, gave what was probably the first definition of an ideal solution as: "an ideal solution is distinguished by the facts that no heat is evolved or absorbed and no change of volume occurs when it is diluted."

Several authors since have dealt with ideal solutions including especially G. N. Lewis and Hildebrand² who, in his recent monograph, says: "We may, therefore, follow G. N. Lewis in defining an ideal solution as one which obeys Raoult's law

$$\frac{p_0 - p_1}{p_0} = \frac{n}{N + n}$$

at all concentrations and pressures, a definition which has some important consequences. It follows from it, as Lewis has shown, that the formation of such a solution will take place from its component liquids without any heat of mixing and without any change in volume."

Washburn³ expresses the same relation in a slightly different form as $p_A = p_{0A} X_A$, defining the terms in the statement: "The partial pressure

¹ Z. physik Chem., 31, 22 (1899).

² "Solubility", 59 (1924).

³ "Principles of Physical Chemistry", 144 (1915).

of any molecular species above an ideal solution is equal to its vapor pressure as a pure liquid multiplied by its molecular fraction in the solution. In other words, the partial vapor pressure of any molecular species from an ideal solution is a linear function of its molecular fraction in that solution."

At this point, it might be well to add one more characteristic of the ideal solution which, although it is not always introduced into the discussion, may be of more fundamental importance than the others mentioned. If we generalize the ideal solution equation to avoid the confusion of solute and solvent using the definition of an ideal solution as just given, the relation may be written:

$$P_A = P_{0A} \frac{N_A}{N_A + N_B}$$

where N_A represents the number of mols of A dissolving in N_B mols of B and where P_A is the partial pressure of A over the solution and P_{0A} the partial pressure of pure A. For the dilute solution when N_A is small compared with N_B , this may be come:

$$P_A = P_{0A} \frac{N_A}{N_B}$$

$$\text{But } N_B = \frac{\text{volume of B used}}{\text{molecular vol. of B}} = \frac{V}{(M.V.)_B}$$

and consequently

$$P_A = P_{0A} (M.V.)_B \frac{N_A}{V}$$

For definite pairs of substances A and B, the values of P_{0A} and $(M.V.)_B$ are constants over the whole range of solubility. Therefore, we may write

$$P^A = K \frac{N_A}{V_B}$$

where, it is emphasized $K = P_{0A} (M.V.)_B$ and so is at once calculable for a given solution. But $P_A = K \frac{N_A}{V_B}$ is similar to the general form of Henry's law

which is usually written $p = kc$. In so far as the equation just derived is of the form of Henry's law, we may follow van't Hoff¹ who showed that "we may conclude that gases which on solution follow Henry's law, possess the same molecular weight in the solution as in the gaseous state, with only the possible exception that hydrate formation, always without change in size of the gaseous molecule, may occur."

The same result might have been arrived at in another way. In so far as a given substance A dissolves in B according to a linear relation between pressure and concentration, it follows Henry's law. In case this straight line coincides with the straight line drawn from zero to the vapor pressure of pure A, the solution is said to be ideal. Consequently the case of the ideal solution is a special case of Henry's law, which latter may be represented by a straight line of unpredictable slope, while the slope of the line for the ideal solution

¹ "Lectures on Theoretical Chemistry" 31 (1899).

has a very definite value. Consequently, since the ideal solution is a special case of Henry's law, and since any solution which follows Henry's law has as its necessary characteristic that the molecular weight of the solute must be the same in the solution as in the vapor, this is to be added to the definition of the ideal solution.

We may therefore summarize our definition of an ideal solution as one whose formation is accompanied by no heat changes, and whose volume represents the sum of the volumes of its components before mixing—that is there are no volume changes. Furthermore, the partial pressure of each component is equal to its vapor pressure as a pure substance multiplied by its mol fraction in the solution and, lastly, the molecular weight of each component in the solution is the same as in the vapor above the solution. Then for the ideal solution according to Washburn,

$$p_1 = p_0 \frac{N}{N + n}$$

or

$$\frac{p_0}{p_1} = \frac{N + n}{N}$$

which is the form that will be used extensively later in the paper. Consequently we may write for the ideal solution Form I as:

$$PV_m = RT \ln \frac{N + n}{N}$$

and Form II as:

$$PV_1 = \frac{N}{n} RT \ln \frac{N + n}{N}$$

Also from $\frac{p_1}{p_0} = \frac{N}{N + n}$ we may get $1 - \frac{p_1}{p_0} = 1 - \frac{N}{N + n}$.

and consequently

$$\frac{p_0 - p_1}{p_0} = \frac{n}{N + n}$$

This is the form previously referred to as Raoult's law and is the relation Raoult claims to have arrived at empirically as a result of study of his brilliant vapor pressure measurements. It is therefore clear that the definitions by Washburn and by Lewis are equivalent and are capable of being derived from each other.

It would be well before proceeding further to point out that, although in the above development, we have shown that for a specific gas and a specific liquid, ideal solution properties permit the ideal solution equation to be converted into a form similar to Henry's law, these two relations are not equivalent. For definiteness these are here set down. Raoult's equation is

$$p_A = p_{0A} \frac{N_A}{N_A + N_B}$$

and Henry's law is expressed by $p = kc$.

The temptation is great to say the two forms are equivalent term for term but this is not true. The term p_0 is a perfectly definite, usually measurable, quantity, while the k of Henry's law is to be revealed only experimentally.

So far, Henry's law has been shown to be true only for dilute solutions. For such solutions there would be no change in its form if, instead of volume concentrations (grams per cc.), we substitute mass concentrations so that it might become:

$$p = k_1 \frac{N_A}{N_B}$$

where N_A and N_B represent mols of solute and solvent respectively. For the dilute solutions the difference is negligible between this form and

$$p = k_2 \frac{N_A}{N_A + N_B}$$

It is quite possible that this is the form in which Henry's law ought always to be expressed; but, so far, this has not been stated explicitly.¹ If we assume definitely that $k_2 = p_{0A}$, then we shall have idealized Henry's law into the expression of Raoult's law. In order to do this, however, it has been necessary to change the volume concentrations of Henry's law into the mass concentrations of Raoult's law. This change is not particularly significant in the dilute solutions to which Henry's law applies. It is important, however, that the specific constant of Henry's law must be replaced by the general constant of Raoult's law. It will be shown below that this cannot be done. Furthermore it is clear that for a gas above its critical temperature p_{0A} can have no physical significance.

Consider the case of a single gas dissolving in two or more different liquids under the same partial pressure of the gas above a fixed volume of liquid. The idealization of Henry's law into Raoult's law as indicated above, gives for the ideal solution

$$p = \frac{p_{0A}(M.V.)_B}{M_A} \frac{g_A}{V_B},$$

where g_A/V_B is the C of Henry's law, $(M.V.)_B$ the mol volume of liquid B and M_A the molecular weight of A. Then g_A ought to be inversely proportional to $(M.V.)_B$. In other words, if a gas in dissolving follows Henry's law, and if Henry's law is equivalent to the ideal solution equation of Raoult, then the solubility of the gas ought to be inversely proportional to the molecular volume of the absorbing liquid.

This may also be shown in the symbols previously used in this paper. For the ideal solution of the same gas in various liquids $p = p_0 \frac{n}{N + n}$. In the experiment the value of p , the partial pressure of the gas over the solution may be kept constant; p_0 will also be constant. Therefore $\frac{n_1}{N_1 + n_1} = \frac{n_2}{N_2 + n_2}$, where the subscripts refer to the two different solutions. This relation gives

$$\frac{n_1}{n_2} = \frac{N_1}{N_2}$$

¹ If Henry's law is to be expressed in mass concentrations, the distribution law must also be so expressed.

But since $N_1 = \frac{\text{volume of absorbing liquid (1)}}{\text{molecular volume of liquid (1)}}$

and $N_2 = \frac{\text{volume of absorbing liquid (2)}}{\text{molecular volume of liquid (2)'}}$

if we use the same volume of absorbing liquid in each case, say 1 cc. the ratio of molecular solubilities of the gas in the two liquids is:

$$\frac{n_1}{n_2} = \frac{g_1}{g_2} = \frac{\text{mol volume of liquid (2)}}{\text{mol volume of liquid (1)}}$$

as was found before. It will be well to test this relation for some experimental cases.

Data for testing this relationship will be found in a study of the absorption of gases in petroleum by Gniewosz and Walfisz.¹ It is readily admitted that we have no knowledge of the molecular weight or volume of petroleum. But if we compare the absorption coefficients of the same gases in petroleum and in water, we need to take into account the molecular volume of neither. The ratio of the absorption coefficients ought to be a constant if the idealization of Henry's law is justified.

TABLE I
Absorption Coefficients at 20°

| | (1) For Petroleum | (2) For Water | (1)/(2) Ratio |
|-------------------------------|----------------------|------------------|------------------|
| H ₂ | 0.0582 | 0.0193 | 3.02 |
| N ₂ | 0.117 | 0.0140 | 8.36 |
| O ₂ | 0.202 | 0.0284 | 7.11 |
| N ₂ O | 2.11 | 0.670 | 3.15 |
| C ₂ H ₄ | 0.142 | 0.149 | 0.95 |
| CO ₂ | 1.17 | 0.901 | 1.3 |
| CO | 0.123 | 0.0231 | 5.3 |
| CH ₄ | 0.131 | 0.0350 | 3.7 |

It may be objected, however, that we cannot test this relation truly by reference to water because water is an abnormal liquid. For answer to that is brought the evidence collected by Woukoloff² who found the solubility of carbon dioxide in 1 cc. of carbon disulphide to be 0.844 cc., while 1 cc. of chloroform absorbs 2.758 cc. of carbon dioxide, the gas being in each case reduced to standard conditions and the absorption taking place in each case under a pressure of 478 mm. The molecular volume of carbon disulphide is about 80 cc. and of chloroform about 60 cc. but the absorption coefficients of 0.844 and 2.75 would hardly seem to be in inverse proportion to the molecular volumes.

¹ Z. physik. Chem., 1, 70 (1887).

² Compt. rend., 108, 674 (1889); 109, 61 (1889).

It seems evident, then, that Henry's law and Raoult's law are not equivalent. The constant in Henry's law may contain p_{0A} , $(M.V.)_B$, and M_A as has been shown above. In addition, however, it must contain some other factor whose nature is as yet unknown and which will represent the specific character of solubilities. Experimentally some liquids follow Raoult's empirical relation, while some gases in liquids follow Henry's law, also empirical. As yet no system is known which follows both simultaneously.

Considerable space has been given to this demonstration because some modern authors have treated these equations as equivalent, deriving Raoult's law from Henry's law. Frazer's derivation is a case in point.¹

"Since the pressure of a gas is proportional to the number of particles present per unit volume, the vapor pressure of a liquid due to any molecular species present, will be proportional to the number of particles of this molecular species present in the liquid

$$p = k \frac{N}{N + n}."$$

In other words, an ideal solution is postulated and put into the form of Henry's law using mass concentrations. The specific factor of Henry's law is then disregarded and k is set equal to p_0 . Naturally Raoult's law follows, since it was put in as the original assumption. One may well doubt also if association of the solvent has no effect and if the solute effect on displacement of the solvent equilibrium might not influence the relation, though it is explicitly stated that in an associated liquid like water the same relationship is true.

We can now come back to the relation $PV = RT$. Ever since van't Hoff showed that an analogy existed between the osmotic pressure of a solution and the gaseous pressure which would be exerted by the solute, and that both could be expressed as $PV = RT$, the V to be used has been the object of much speculation and the subject of considerable controversy. Probably the most commonly used value of V has been the volume of the solution containing one mol of solute. Van't Hoff made it quite definite that the solutions with which he proposed to deal were, "solutions so dilute as to be comparable with ideal or perfect gases, in which the action on one another of the dissolved molecules, as well as their actual volume compared with that of the space they inhabit, is so small as to be negligible." At best then, van't Hoff expected $PV = RT$ to have validity only for the very dilute solutions and he would not have been at all surprised that it failed for solutions of such concentrations as have been measured.

This approximation form has some value, however, if it be written $PV_1 = RT$. For such dilute solutions as those for which this is valid, we obtain from Form II

$$\frac{n}{N} = \ln \frac{p_0}{p_1}$$

¹ Taylor: "Treatise on Physical Chemistry," 1, 237 (1924).

which is a relation fundamental to the determination of molecular weights from freezing points or boiling points of solutions. The basic equation is that of Clausius-Clapeyron

$$\frac{d \ln p}{dT} = \frac{Q}{RT^2}$$

where Q is the latent heat of fusion or of vaporization of the pure solvent.

Substituting for $d \ln p$ its equal $\frac{n}{N}$, we have $\frac{n}{N} = \frac{QdT}{RT^2}$

But $n = g/M$, and for any given experiment with a fixed amount of a given solvent $\frac{QN}{RT^2}$ is a constant. Therefore $M = \frac{Kg}{dT}$ which is the usual equation used for the calculation of molecular weights, where K is the boiling point or freezing point constant. It follows then, that in so far as $PV_1 = RT$ is valid, $\frac{n}{N} = \ln \frac{p_0}{p_1}$ and molecular weights can be determined as shown above.

Both $PV_1 = RT$ and $PV = RT$ are justifiable approximations for dilute solutions. The former is in some cases the better form, yet $PV_1 = RT$ is always an approximation and will deviate from the facts more and more as the concentration of the solute increases. The extent of this deviation may be shown by reference to Form II as here derived,

$$PV_1 = RT \frac{N}{n} \ln \frac{p_0}{p_1},$$

or better yet by the form taken by this equation if we assume that we are dealing with an ideal solution. Form II then becomes Form IV

$$PV_1 = RT \frac{N}{n} \ln \frac{N+n}{N} \quad (IV)$$

since $\frac{p_0}{p_1} = \frac{N+n}{N}$. The case of the infinitely dilute solution may be considered, where n approaches zero.

$$\frac{N}{n} \ln \frac{N+n}{N} \text{ may be written } \frac{N}{n} \ln \left(1 + \frac{n}{N} \right)$$

On expansion, we obtain;

$$\ln \left(1 + \frac{n}{N} \right) = \frac{n}{N} - \frac{n^2}{2N^2} + \dots \text{ in powers of } n$$

Hence the expression becomes

$$\frac{N}{n} \left[\frac{n}{N} - \frac{n^2}{2N^2} + \dots \right]$$

which equals one as n approaches zero, and $\frac{n^2}{2N^2}$ and the succeeding terms of the expansion become negligible.

The evaluation of $\frac{N}{n} \ln \frac{N+n}{N}$ as n approaches zero is due to Professor

Virgil Snyder of the Cornell University Department of Mathematics. Since this term equals one as n becomes infinitely small, it follows that for the infinitely dilute solution $PV_1 = RT$.

For any finite value of n , the osmotic pressure calculated from $PV_1 = RT$ for an ideal solution will be too large since for finite values of n , $\frac{N}{n} \ln \frac{N+n}{N}$ will always be less than unity as shown in the development above when $\frac{n^2}{2N^2}$ and the succeeding terms of the expansion can no longer be neglected. So, for example, for the case when $N = 9n$ the value of $\frac{N}{n} \ln \frac{N+n}{N}$ will be 0.948 and when the solution is made up of two mols of solute to eight mols of solvent $\frac{N}{n} \ln \frac{N+n}{N}$ becomes 0.892. This all assumes an ideal solution and means that the osmotic pressure calculated from $PV_1 = RT$ when the solute molecules constitute 10 percent of all the molecules present, will be about 5 percent larger than the osmotic pressure calculated from the real formula

$$PV_1 = RT \frac{N}{n} \ln \frac{N+n}{N}$$

since for this concentration, actually $PV_1 = 0.948 RT$. For aqueous solutions, some of which experimentally appear to behave something like ideal solutions, this means a concentration of about 6.2 molar which is more than the solubility of most solutes in water. Therefore we may say that below this concentration, in so far as a given solution is ideal, we can express its osmotic pressure by $PV_1 = RT$ with less than five percent error.

The relation may be shown in another way. Suppose the data N , n , and V_1 be shown for a given ideal solution. What will be the error involved in calculating the osmotic pressure from $PV_1 = RT$? The actual osmotic pressure would be given by the full equation

$$PV_1 = RT \frac{N}{n} \ln \frac{N+n}{N},$$

while the approximate value would be given by

$$P_A V_1 = RT.$$

Dividing the first equation by the second we have:

$$\frac{P}{P_A} = \frac{N}{n} \ln \frac{N+n}{N}$$

or

$$P = P_A \frac{N}{n} \ln \frac{N+n}{N}$$

In other words, P_A as calculated from the approximate $PV_1 = RT$ equation will always be larger than the actual P of the ideal solution since for any finite value of n , $\frac{N}{n} \ln \frac{N+n}{N}$ is always less than one. When $\frac{N}{n} = 9$ this value

is 0.948 and when $\frac{N}{n} = 4$ this value becomes 0.892. If necessary, we may drop the assumption of ideal solutions and more generally write

$$P = P_A \frac{N}{n} \ln \frac{p_0}{p_1}$$

which will probably have the same sort of value as in the ideal case.

This relation is interesting in view of the work of Swietoslawski¹ who discusses "Deviations from van't Hoff's Law." He treats $PV = RT$ as van't Hoff's law and tries to add correcting terms to this equation expressed as $P = nRT$ where n is the mols of solute in one cc. of solution. He gives Form I as here derived as having been derived thermodynamically as

$$P = \frac{RT}{V} \ln \frac{p_0}{p_1}$$

It will be seen that there is no molecular weight term, which should surely be included unless the R he has in mind be a specific gas constant R referring to one gram rather than one mol of gas. Also he defines V as the specific volume of the pure solvent which cannot be true. His suggestion to improve the applicability of $P = nRT$ is to change it to $P = xznRT$ where x is a measure of deviation of the solution from Raoult's law and z is a function of the relative molecular volumes of solute and solvent. It will be clear then, that, in so far as Swietoslawski used the volume of solution, he was not using van't Hoff's law for osmotic pressure and if he had used $PV_1 = RT$ as here indicated, the difference between the osmotic pressure by this formula and by the accurate formula would not be influenced by the function z .

The z value of Swietoslawski does become a factor however if, as he does, $PV = RT$ is used, where V is the volume of solution. Form II is

$$PV_1 = RT \frac{N}{n} \ln \frac{p_0}{p_1}$$

If, in deriving Form II, we had pressed out not that volume (V_1) of solvent containing one mol of solute but a volume V of solvent equal to the volume of the solvent V_1 , plus the volume of one mol of solute (MV_1), the expression for Form II would have been

$$PV = \left(\frac{N}{n} + \frac{(M.V.)_1}{(M.V.)_2} \right) RT \ln \frac{p_0}{p_1}, \quad (V)$$

which we shall denote by Form V. It is seen that this V is the volume of solution containing one mol of solute, and is equal to the volume of solvent containing one mol of solute plus the volume of one mol of solute. This added volume of solvent pressed out will equal the $\frac{(M.V.)_1}{(M.V.)_2}$ mols of solvent where

$(M.V.)_1$ is the mol volume of solute and $(M.V.)_2$ is the mol volume of solvent.

For dilute solutions $PV_1 = RT$ is a justified approximation and for these same dilute solutions $PV = RT$ will differ little from it. From Form V, in so far as $PV = RT$ experimentally

¹ Bull., (4) 37, 263 (1925).

$$\left(\frac{N}{n} + \frac{(M.V.)_1}{(M.V.)_2} \right) \ln \frac{p_0}{p_1} = 1$$

or

$$\frac{n}{N + \frac{(M.V.)_1}{(M.V.)_2} n} = \ln \frac{p_0}{p_1}$$

But for dilute solutions,

$$\ln \frac{p_0}{p_1} = \frac{p_0 - p_1}{p_0}$$

approximately. Therefore we have what appears to be a more accurate statement of Raoult's law derived from these equations,

$$\frac{n}{N + \frac{(M.V.)_1}{(M.V.)_2} n} = \frac{p_0 - p_1}{p_0}$$

When the mol volume of the solute $(M.V.)_1$ is equal to the mol volume of the solvent $(M.V.)_2$, this expression is exactly that arrived at empirically by Raoult. In order to justify it, Raoult had to confine himself to dilute solutions experimentally just as has now been done in its derivation.

It will be seen at once that this expression involves a larger error than would have been introduced by assuming $PV_1 = RT$. In so far as this is true, we get from Form II

$$\frac{n}{N} = \ln \frac{p_0}{p_1} \quad (VI)$$

which is more accurate than the expression above including the mol volumes of the components.

Equation VI for dilute solutions gives

$$\frac{n}{N} = \frac{p_0 - p_1}{p_0}$$

which is the form Kendall¹ calls the "dilute-solution" equation, and he adds: "This relation is strictly valid only for solutions of infinite dilution, constituting the limiting case of the more exact equation: $\frac{n}{N} = \ln \frac{p_0}{p_1}$. The difference

between the calculated values for the two forms of the equation is, however, inappreciable even for a fairly concentrated solution."

It may be pointed out that $\frac{n}{N} = \ln \frac{p_0}{p_1}$ offers a method of finding the molecular weight of the solute in the solution or the solvent in the vapor. This method is perfectly valid only for the dilute ideal solution. In every other case $PV_1 = RT$ does not hold even approximately and should be replaced by $PV_1 = RT + f(Q)$ where Q is the heat of dilution and as yet the function is unknown. In so far as $f(Q)$ does not equal zero, as it does in the ideal solution, $\frac{n}{N} = \ln \frac{p_0}{p_1}$ will not serve for molecular weight determinations except by consideration of its effect.

¹ J. Am. Chem. Soc., 43, 1391 (1921).

In spite of the fact that osmotic pressures for a solution as calculated from $PV_1 = RT$ differ from the accurate value by a factor that contains no volume term and is not affected by the relative mol volumes of the solute and solvent, the accurate value of osmotic pressure does depend on the molecular volume of the solvent. Consider two ideal solutions of the same substance in different solvents A and B, the concentrations being such that $\frac{N}{n}$ is the same for both solutions. Then the values of $\ln \frac{N+n}{N}$ will be the same in the two solutions and the osmotic pressures of the two solutions will be represented by

$$P_A V_{MA} = RT \ln \frac{N+n}{N}$$

$$P_B V_{MB} = RT \ln \frac{N+n}{N}$$

where P_A and P_B are the osmotic pressures of the two solutions and V_{MA} and V_{MB} are the mol volumes of solvents A and B respectively.

Dividing, we get

$$P_A V_{MA} = P_B V_{MB}$$

In other words, the osmotic pressures of two ideal solutions at the same temperature and having the same value of $\frac{N}{n}$ are inversely proportional to the mol volumes of the solvents employed. This is just as valid for two non-ideal solutions for which the values of $\ln \frac{p_0}{p_1}$ are the same.

Of those who have attacked the van't Hoff equation for osmotic pressure, probably none has been more influential than G. N. Lewis.¹ In reviewing the situation, he discusses the inadequacy of the van't Hoff equation which to him has always meant $PV = RT$ where V is the volume of the solution containing one mol of the solute. Quite naturally it is easy to show that this equation does not represent the experimental facts over any large concentration range. Morse and Frazer² had improved the situation very appreciably by changing the volume of the solution empirically to mean the volume of the solvent water at its maximum density. This gave rather good agreement on their sugar solutions up to molar concentrations since that volume of solution differed but little from V_1 , which should have been introduced as here defined. No intimation is given that van't Hoff did derive perfectly accurate and general equations for the osmotic pressure. Instead, since $PV = RT$ as usually defined is of so little value and since even the modification of Morse and Frazer leaves much to be desired, Lewis proposes to discard the so-called van't Hoff equation $PV = RT$ and substitute for it in the study of solutions, Raoult's empirical law $\frac{p_0 - p_1}{p_0} = \frac{n}{N+n}$ which, although it has as yet no theoretical explanation does fit the facts remarkably well for a number of solutions.

¹ J. Am. Chem. Soc., 30, 668 (1908).

² Am. Chem. J., 34, 1 (1905).

Lewis then proceeds thermodynamically to derive an expression,

$$P - \frac{\alpha P^2}{2} = \frac{RT}{V_0} \ln \frac{p_0}{p_1} \quad (\text{III})$$

where " α is the coefficient of compressibility of the solvent, V_0 is its molecular volume," and the other terms are as we have previously defined them. This compressibility term will be shown later to be foreign to the discussion. If it is negligible and if V_0 be equivalent to V_M as defined in this paper, then Lewis' equation is the same as Form I. Lewis then proceeds to define the

perfect solution as one which obeys Raoult's law, $p_1 = p_0 \frac{N}{N+n}$. The thermodynamic equation then becomes, for the ideal solution

$$P - \frac{\alpha P^2}{2} = \frac{RT}{V_0} \ln \frac{N+n}{N} \quad (\text{VII})$$

Using this last equation, the calculated osmotic pressures for the sugar solutions of Morse and Frazer agree much better with the observed values than do the values calculated by the old $PV = RT$. It is observed that Lewis' new values are, in eight cases out of ten, farther from the observed values than are those calculated by Morse and Frazer. These solutions however, are normal or less, so the ideal equation is next applied to some solutions which Zawidski¹ has shown from vapor pressure measurements are ideal over the whole range. Lewis' Table V is here presented as Table II:

TABLE II
 $C_2H_4Cl_2$ in C_6H_6 at 50°

| n | p_1 | P van't Hoff | P Morse and Frazer | P Lewis | P Found |
|-------|-------|-----------------|-----------------------------|------------|------------|
| 0.0 | 268.0 | — | — | — | — |
| 0.293 | 268.0 | 91 | 120 | 101 | 100 |
| 0.416 | 156.0 | 128 | 205 | 157 | 158 |
| 0.522 | 127.8 | 160 | 315 | 215 | 217 |
| 0.657 | 92.4 | 196 | 549 | 313 | 310 |
| 0.754 | 65.9 | 223 | 880 | 413 | 406 |
| 0.920 | 21.8 | 268 | 3290 | 743 | 735 |

In Table II the first column gives the mol fraction of solute; the second, the partial vapor pressure of the solvent, taken from Zawidski; the third, the osmotic pressure calculated by the van't Hoff equation; the fourth, that calculated by the equation of Morse and Frazer; the fifth, that calculated by equation (VII) (the equation above), while the last column gives the actual osmotic pressure obtained thermodynamically from the vapor pressures by means of equation (III), (the general equation above). Lewis concluded, "We see from these Tables how closely in these two cases the actual osmotic

¹ Z. physik Chem., 35, 129 (1900).

pressures agree with those calculated by equation (VII) and how far from the truth are the pressures calculated both by the van't Hoff equation and by that of Morse and Frazer."

Several interesting observations may be made concerning the Table. Of the compressibility term, Lewis says, "The second term in equation (VII) or (III) except at the very highest concentrations, is comparatively insignificant, amounting usually to only a few per cent of the value of P even when the osmotic pressure is as high as a thousand atmospheres." For the ideal solution V_0 is equal to V_M as here defined. Consequently the two equations given are practically the ones that van't Hoff gave and the same as Form I here derived. Therefore the osmotic pressures set down in the last column can be accepted as correct. The failure of those calculated by Lewis to agree with these will, by reference to equations (VII) and (III), be seen to be due

entirely to the fact that $\ln \frac{p_0}{p_1}$ does not exactly equal $\ln \frac{N+n}{N}$. In other words,

the solution of ethylene chloride in benzene is not quite an ideal solution and these equations afford a rather round-about way to demonstrate that. No advance is made over the van't Hoff or thermodynamic formula for the accurate calculation of osmotic pressures of concentrated solutions.

In the second place, it is quite evident that the equation $PV = RT$ where V is the volume of solution cannot express the facts and there is no good reason why it should be valid beyond the infinitely dilute solutions.

Finally, it may be observed that the values calculated by Morse and Frazer's method are increasingly higher than the actual osmotic pressures. For the ideal solution under discussion the volume of pure solvent is exactly equal to V_1 as here defined. Therefore, for the ideal case, the equation of Morse and Frazer is $PV_1 = RT$. It has already been shown why this equation yields values of P that are increasingly higher than the actual values; as the

value of $\frac{N}{n} \ln \frac{N+n}{N}$ the neglected term, gets smaller with increase in concentration, and if this be neglected the calculated value of P becomes increasingly larger.

The above discussion will also throw light on another objection made to what Lewis calls the van't Hoff equation. Hildebrand¹ recently expressed this objection on the ground that "it leads to absurd figures, for, as the proportion of solvent in the solution approaches zero, the osmotic pressure actually approaches infinity, while according to the equation of van't Hoff it should never exceed a few hundred atmospheres." Hildebrand is making the common mistake of substituting V the volume of the solution in which one gram molecular weight of the solute is dissolved for what we have called V_1 , the volume of the solvent in which one gram molecular weight of the solute is dissolved. The two are identical for infinitely dilute solutions, but not necessarily so for any other concentration. For the concentrated solutions

¹"Solubility," 26 (1924).

V_1 becomes infinitely small and P therefore may go to infinitely large values. It should be clearly understood, however, that an equation of the form $PV = RT$ cannot accurately express osmotic pressures over any wide range of concentrations, no matter what definition be given the V . If V_1 be used instead of volume of solution, the range is increased and the error is readily calculable for the ideal solution.

There is however no limit to the applicability of Forms I and II as here derived except the assumptions introduced into their derivations. They are valid for solutions of any concentration, so long as the solvent vapor over the solution can be regarded as a perfect gas. This means that the real equations of van't Hoff do meet the second objection of Lewis and Hildebrand and do permit the calculation of infinite values of P for infinite concentration of the solution. In Form I, $\ln \frac{p_0}{p_1}$ approaches infinity for infinitely concentrated solutions and therefore P may have infinitely large values since $\frac{RT}{V_M}$ is practically a constant. The same result is obtained from Form IV,

$$PV_1 = RT \frac{N}{n} \ln \frac{N+n}{N}. \quad (\text{IV})$$

Calculation shows that as $\frac{N}{n}$ decreases (concentration increases), the value of V_1 decreases much more rapidly than does $\frac{N}{n} \ln \frac{N+n}{N}$. Consequently P must increase very rapidly and approach infinity for infinitely small values of $\frac{N}{n}$ (infinite concentration).

Before leaving these observations on the formula the matter of compressibility ought to be discussed. In addition to Lewis, Porter, Berkeley, and others have added to our Form I a compressibility term $\pm \frac{\alpha P_2}{2}$ where α is the compressibility of the pure solvent. If Form I,

$$PV_s = \frac{RT}{M_2} \ln \frac{p_0}{p_1}$$

expresses the relation, then no further term is required. But if the value of V_s of the formula changes with osmotic pressure some correction will be required, for the observed osmotic pressure will be greater than it would be if V_s were constant.

It is first offered that one could not hope to compress water by a piston permeable to water, and it is not readily apparent why the sugar makes any difference. In other words a variation of osmotic pressure because of solvent compressibility implies that when pressure is put on a sugar solution by means of a piston permeable to the water, the water is compressed.

To show this in another way, an analogy may be resorted to. If a mixture of nitrogen and hydrogen were separated from pure hydrogen by a wall permeable only to hydrogen, and if pressure were applied to the mixture,

hydrogen would pass through from the mixture to the pure hydrogen until its partial pressure in the mixture would be the same as in the pure hydrogen. This means that the hydrogen would not be compressed—its volume concentration remains constant in the mixture. The nitrogen however is compressed. It is suggested that this is analogous to the situation in a solution and that there only the solute is compressed by pressure applied through a piston permeable to the solvent.

The Evolution of the Ideal Solution Equation

The modern treatment of the theories of solutions owes much to the historic researches of F. M. Raoult who measured the freezing points and vapor pressures of a great many solutions in various solvents and from the results for dilute solutions expressed the relation between vapor pressure and concentration in the law that bears his name. This law is usually expressed

mathematically as $\frac{p_0 - p_1}{p_0} = \frac{n}{N + n}$ and is put in words by the statement that

the relative lowering of the vapor pressure of a pure solvent is equal to the mol fraction of the solute in the solution. The various papers of Raoult would indicate that he arrived at this law empirically as the one best expressing his experimental results for dilute solutions; but further study reveals that he was probably aided largely in deriving the generalization by the contemporaneous theoretical work of van't Hoff.

The earliest reported work of Raoult¹ on the vapor pressures of solutions had to do with the relation that was found to exist between the lowering of the freezing point, and the lowering of the vapor pressure at 100° C by the same aqueous solutions. The result of these experiments was that for concentrations of one gram of salt per 100 grams of water

$$7.6\Delta = p_0 - p_1$$

where Δ represented the freezing-point lowering and $p_0 - p_1$ the vapor pressure lowering due to the salt. The fact that this formula comes out so simply is a result of coincidence that the molecular lowering for solutions in water is nearly the same as the molecular weight of water. This will be elaborated further when the formula as finally reached is developed.

Another result of this paper was that solutions of salts in water were shown to contain too many disturbing factors for effective generalization so that for several years Raoult worked on solutions of various solutes in organic solvents or of organic solutes in water. The freezing points of many of the latter type of solutions were measured² and it was found that the molecular lowerings of the various organic solutes in water were practically identical and averaged about 18.5°.

In the same year,³ the freezing-point investigations were extended to various organic solvents and molecular lowerings were reported as follows: in water

¹ Compt. rend., 87, 167 (1878).

² Compt. rend., 94, 1517 (1882).

³ Compt. rend., 95, 187 (1882).

37; formic acid 28; acetic acid 39; benzene 49; nitrobenzene 70.5; and ethylene bromide 117.

In each case, except that of water as solvent, if these lowerings produced by one mol of solute in 100 grams of solvent were divided by the formula weight of the solvent, the quotient came out approximately 0.62. Raoult generalized this to mean that a molecule of any compound dissolving in 100 molecules of any liquid lowers the freezing point about 0.62 degrees. The case of water was very perturbing for the quotient for water came out 2.05. This Raoult explained by suggesting that the "physical molecule must be

made up of two or three chemical ones" because $\frac{37}{54} = 0.685$ which was of the

order of 0.62. It should be added that in all the solvents listed above, Raoult found values of the molecular lowering that grouped themselves about two average values, the one being double the other. The molecular lowerings listed above are all the double values which Raoult believed to be normal while the others were abnormal. He was not exactly consistent in this for in a later paper¹ he discusses the value of the freezing-points for determining

the molecular weight of the solute and sets the equation as, $M = \frac{19}{A}$, when M

is the molecular weight of the solute, A is the grams of solute per 100 grams of water and 19 is the molecular freezing-point lowering of water. In the next year, he reported freezing-point lowerings in thymol and naphthalene as solvents stating that the value 0.62 is also valid for them.

In a longer paper, published in 1884, Raoult¹ gives some slightly different numerical data, Table III.

TABLE III

| Solvent | Mol. Wt. Solvent | Maximum molecular lowering, 1 mol per 100 g | Molecular lowering 1 mol per 100 mol |
|--------------------|------------------|---------------------------------------------|--------------------------------------|
| Water | 18 | 47 | 2.61° |
| Formic Acid | 46 | 29 | 0.63 |
| Acetic Acid | 60 | 39 | 0.65 |
| Benzene | 78 | 50 | 0.64 |
| Nitrobenzene | 123 | 73 | 0.59 |
| Ethylene dibromide | 188 | 119 | 0.63 |

Raoult points out that, with the exception of water, the molecular lowering varies only from 0.59° to 0.65° with a mean value of 0.63°. "Water is the only exception; but that is not surprising for a liquid which shows many other peculiarities and it is permissible to explain the anomaly by assuming that each of the physical molecules, of which it is formed, consists of several chemical molecules united together. At a time when I had only obtained a small

¹ Compt. rend., 101, 1056 (1885).

number of molecular lowerings higher than the mean lowering of 37 in aqueous solutions, I believed that the physical molecules of water were composed of three chemical ones. In fact, if we divide 37 by 18×3 , we get as quotient 0.685 which is not very far from the mean quotient of 0.63 obtained with the other solvents. I have called attention to this in an earlier paper.¹ But new determinations make it no longer possible to consider the molecular lowerings distinctly higher than 37 as doubtful. I am, therefore, compelled to recognize that molecular lowerings in water may really rise to 47, a maximum value in many cases where the dissolved substances do not decompose. To explain such a lowering, it is sufficient to assume that the molecules of water are united in fours, at least near zero. The quotient of 47 by 18×4 is 0.65, a number remarkably close to the mean value of 0.63 obtained with the other solvents."

The molecular lowering of 47 is obtained with potassium ferrocyanide, barium chloride, potassium oxalate, etc. It is quite evident that Raoult had not decided which were the normal lowerings and that he believed that the molecular weight of the solvent as liquid was a factor. Some people still think so. It is also interesting to note that at this time he considered acetic acid as normal as benzene. Of course the real difficulty is that the value of 0.63 has no theoretical significance. It is purely a coincidence that acetic acid gives 0.65, postulating a molecular weight of 60.

There were a few more papers confirming and extending the work on cryoscopy but it was gradually neglected and the measurements of vapor pressures resumed. On Dec. 6, 1886 it was reported² that "if one dissolves one molecular weight of any compound in 100 gms. of ether, the vapor pressure of the liquid is diminished by a constant fraction of its normal value; this fraction is about 0.71 at all temperatures between 0° and 25°." This was formulated mathematically into

$$\frac{p_0 - p_1}{p_0} \times \frac{M_1}{P} = K$$

where M_1 is the molecular weight of the solute, P is the number of grams of solute in 100 grams of ether and K is practically a constant varying between 0.67 and 0.74 with 0.71 as its mean value. On April 4, 1887, it was reported³ that up to 7 mols of solute per 100 grams of ether, the lowering of the vapor pressure can be expressed by the formula

$$\frac{p_0 - p_1}{p_0} \frac{M}{P \times 74} = D$$

where 74 is the molecular weight of ether and D is a constant whose value is approximately 0.0096. Further study of other solvents led to the statement⁴ read on May 23, 1887 to the effect that "one mol of solute, not a salt, dis-

¹ Compt. rend., 95, 1030 (1882).

² Compt. rend., 103, 1125 (1886).

³ Compt. rend., 104, 976 (1887).

⁴ Compt. rend., 104, 1430 (1887).

solving in 100 mols of any solvent lowers the vapor pressure of the liquid by a fraction nearly constant and about 0.0105." This is equivalent to replacing the 74 in the equation above by the molecular weight of the solvent under discussion, and is the nearest Raoult had come to the earlier formula usually attributed to him. Raoult never found D of the above formula to be 0.0100 but gave values that varied in different solvents between 0.0096 and 0.0105. If however we may assume 0.0100 to be a fair average, we may write the above

equation as

$$\frac{p_0 - p_1}{p_0} = \frac{P}{M_1} \frac{M_2}{100}$$

where $p/M_1 = n$, the mols of solute present and $100/M_1 = N$, the mols of solvent present. This equation then becomes

$$\frac{p_0 - p_1}{p_0} = \frac{n}{N}$$

which Ostwald gave as the earlier form of Raoult's equation, and which had to be given up because of the absurdity it led to when $n = N$ and p_1 had to become equal to zero.

In all this work there had been no reference to van't Hoff whose important paper relative to the vapor pressure of solutions was presented October 14, 1885 before the Swedish Academy and published¹ early in 1886. Van't Hoff had concerned himself greatly with Raoult's work and had calculated Raoult's molecular lowering of the freezing points from the temperature and heat of fusion of the pure solvent arriving at values that on the whole agreed very well with those observed by Raoult. This was taken by van't Hoff as an additional proof that the analogy between osmotic pressure and gaseous pressure was justified.

This work of van't Hoff must have come promptly to Raoult's attention and his next paper,² November 7, 1887 is devoted to a consideration of van't Hoff's work. Raoult points out that van't Hoff has shown on theoretical grounds that "i," the famous van't Hoff correction term, must be calculable from

$$i = 101 \frac{M_1 p_0 - p_1}{M_2 p_0}$$

where $\frac{p_0 - p_1}{p_0}$ is the relative lowering of the vapor pressure by one gram of solute in 100 grams of solvent. Since "i" equals unity for most of the cases with which Raoult has dealt we may write, as he did, $\frac{i}{101} = \frac{M_1 p_0 - p_1}{M_2 p_0}$

But the left hand side of this equation is $\frac{g_1}{g_1 + g_2}$ where g_1 and g_2 represent grams of solute and solvent respectively and in this particular case is equal to 0.0099 which Raoult said was not far from his 0.0105 value experimentally obtained.

¹ Kongl. svenska Vetenskaps Akademiens Handlingar, 21, 3 (1885).

² Compt. rend., 105, 857 (1887).

More light may be shed on this relation by considering that since $\frac{p_0 - p_1}{p_0}$ is the relative lowering in vapor pressure produced by one gram of solute in 100 grams of solvent, $\frac{M_1}{M_2} \frac{p_0 - p_1}{p_0}$ will be the lowering produced by one mol of solute in 100 mols of solvent and this is shown by van't Hoff to be equal to $1/101$. In other words, the complete so-called Raoult law,

$$\frac{n}{N + n} = \frac{p_0 - p_1}{p_0}$$

was in the theoretical derivation of van't Hoff.

It is emphasized that up to the time at which Raoult comments definitely on van't Hoff's work, he had never even stated explicitly the relation $\frac{n}{N} = \frac{p_0 - p_1}{p_0}$, although it was implied in the early paper of 1887. The following year he makes this explicit for some solutions in alcohol which were expressed by $C = \frac{p_0 - p_1}{p_0 n}$ where C is the molecular lowering due to one mol of solute in 100 mols of alcohol and varied from 0.0091 to 0.0110 with a mean value of about 0.0104.

In the same year,¹ however, he did adopt the new form from van't Hoff; but, for most solutions, his data had to be expressed by $\frac{p_0 - p_1}{p_0} = K \frac{n}{N + n}$ where K was a constant varying from 0.70 to 0.90 for solutions of moderate concentrations. For dilute solutions the law had a special expression in that $K = 1$ for dilute solutions. So that, not until a year after Raoult had commented on van't Hoff's theoretical deduction of it, did he arrive at the equation which still bears his name.

Now that we have this statement of the law it would be well to retrace our steps for then we discover that the statement in the first paper here discussed, $7.6\Delta = p_0 - p_1$ is the result of a coincidence and is not fundamental. The later papers on freezing points in aqueous solutions showed that $\Delta = 18.5 \frac{g_1}{M_1}$ where Δ is the depression of freezing point, 18.5 the depression due to one mol of solute in 100 grams of water, g_1 , the weight of solute in 100 grams of water and M_1 its molecular weight. For dilute solutions $\frac{n}{N} = \frac{g_1 M_2}{g_2 M_1} = \frac{p_0 - p_1}{p_0}$ where $g_2/M_2 =$ mols of solvent present. In these experiments $g_2 = 100$ so that $\frac{g_1}{M_1} = \frac{100}{M_2} \frac{p_0 - p_1}{p_0}$. Substituting in the above equation

¹ Z. physik. Chem., 2, 353 (1888).

$$\Delta = 18.5 \frac{100 p_0 - p_1}{M_2 p_0}$$

But for water, $M_2 = 18$ and $p_0 = 760$ at 100° . Therefore, since 18 is so nearly 18.5, the experimental value, we have $7.6 \Delta = \frac{p_0 - p_1}{p_0}$

which is purely accidental. For benzene as solute we should have had

$$7.6 \Delta = \frac{50}{78} (p_0 - p_1)$$

Since it has been shown earlier that $\frac{p_0 - p_1}{p_0}$ is only an approximation for $\ln p_0/p_1$ we may write the true equation for the freezing-point lowering as

$$\Delta = \frac{100 K}{M_2} \ln \frac{p_0}{p_1}$$

At the freezing-point, this will hold for all substances. Since there is no term for the molecular weight of the solute, the relation is true for all solutes, sugar, potassium chloride, sodium sulphate, regardless of dissociation, which is what Raoult found. But it is only when there is no heat of dilution that we are justified in comparing freezing-point lowerings with vapor pressure lowerings at the boiling temperature of the pure liquid.

Before leaving the discussion of Raoult's work, we ought to emphasize that in all of it Raoult considered only the molecular weight of the solvent in the solution. This brought him to grief in the study of solutions in acetic acid.¹ It was found that for twelve different solvents the vapor pressure

lowerings were expressed by $\frac{p_0 - p_1}{p_0} = k \frac{n}{N}$ where k was practically one. But the same eight solutes in acetic acid gave values of k that averaged 1.61 when the molecular weight of acetic acid was taken as 60, its formula weight

As Raoult says, using 60 in the formula is equivalent to assuming that the physical molecule of boiling, liquid, acetic acid contains only a single chemical molecule, $\text{CH}_3\text{CO}_2\text{H}$. "We must seek the cause of this exceptional discrepancy in the considerable error that we make without doubt in taking for the *physical* molecular weight M_1 of liquid acetic acid the value 60 which represents its *chemical* molecular weight. In all probability, at a given temperature, the constitution of the physical molecule of a substance is the same in the liquid state as in the saturated vapor.² If this is really so, the physical molecular weight of boiling, liquid, acetic acid must be equal to $60 \times 3.35/2.08$ or 97."

In a longer paper, published the same year, Raoult³ says much the same thing at greater length. "When dissolved in benzene, nitrobenzene, or ethy-

¹ Raoult and Recoura: Compt. rend., 110, 402 (1890).

² [This is not true for water.]

³ Ann. Chim. Phys., (6) 20, 353 (1890).

lene dibromide, the molecules of acetic acid are formed of two chemical molecules, since the molecular weight of this acid in these solutions is 120 as shown by cryoscopic measurements.

"In the vapor state the same tendency to condensation shows itself. The density of the saturated vapor of acetic acid is much higher than its normal density. This latter is, in fact, 2.08, while the vapor density under atmospheric pressure is, according to M. Cahours, 2.90 at 140°, 3.12 at 130°, and 3.20 at 125°, which, by extrapolation, gives 3.35 for the density of the saturated vapor of acetic acid at the boiling-point, 118°. The mean molecular weight of acetic acid in its saturated vapor is, therefore, at this temperature, $60 \times 3.35/2.08$ or 97, as if this vapor were formed of a mixture of 38 simple molecules and of 62 double molecules.

"If the molecules of the saturated vapor are twinned to some extent, it is probable that those of the liquid formed by their condensation are also twinned, and it is reasonable to assume that the degree of polymerization is the same. According to this hypothesis, the mean molecular weight of M' of liquid acetic acid at the boiling-point, 118°, is 97 just as it is for the saturated vapor.

"If in equation 8 $\left[\frac{f - f'}{f'P} \times \frac{M}{M'} = k \right]$ we make $M' = 97$ instead of $M' =$

60, we find $k = (1.61 \times 60)/97 = 0.997$, just as it should be according to the general law expressed in equation 5

$$\left[\frac{f - f'}{f} \cdot \frac{n + n'}{n} = 1 \right].$$

"This is an important argument in favor of the hypothesis of the identity of molecular constitution of liquids and their saturated vapors at the same temperature, and also in favor of the comprehensiveness of the law announced above, with the limitation that this law applies to the physical molecules as they actually exist in the solution."

When the paper of February 24 was translated into German,¹ van't Hoff appended a note to the translation, explaining that the molecular weight of the solvent in the vapor ought to be introduced. It is not stated either by Raoult or by van't Hoff that van't Hoff had called Raoult's attention to this fact before the first Raoult and Recoura paper appeared; but the paper was presented to the French Academy on February 24 and was published in German on May 23. There is no obvious reason why Raoult should have bothered his head about vapor densities unless it had been suggested to him by van't Hoff. Whether the suggestion came from van't Hoff or not, it was apparently misunderstood by Raoult to mean that the molecular complexity of acetic acid was the same in the liquid and in the vapor. Van't Hoff was quite clear that this is not necessarily so, because he ends his note with the words that "it does not follow from this agreement that liquid acetic acid also shows this abnormal molecular weight."

¹ Raoult and Recoura: *Z. physik. Chem.*, 5, 426 (1890).

It apparently did not occur to Raoult that his conclusion as to the equality of molecular weights in liquid and vapor contradicted his earlier work necessitating the assumption of 36 or 54 for the molecular weight of liquid water, because the vapor density corresponds fairly closely to a molecular weight of 18. It is also interesting to note that Raoult did not even refer to the discrepancy between his present conclusion about acetic acid and his previous one, based on freezing-point lowerings, that acetic acid is just as normal as benzene.

It is clear that in the equation $(p - p')/p = n/(N + n)$, the molecular weight to which N refers is the molecular weight in the vapor. In the case of ideal solutions, the molecular weight is the same in liquid and in vapor; but it is misleading to ignore the theoretical significance of the term.

The conclusions to be drawn from this section are as follows:

1. It has been shown that up to the time when van't Hoff first presented his theoretical treatment of solutions, Raoult had not yet proposed explicitly

$\frac{p_0 - p_1}{p_0} = \frac{n}{N}$ to express the relation between concentration and vapor pressure of a solution.

2. In van't Hoff's equation $i = 101 \frac{M_1}{M_2} \frac{p_0 - p_1}{p_0}$ there is the explicit statement of the ideal solution equation since for such solutions $i = 1$, and $\frac{M_1}{M_2} \frac{p_0 - p_1}{p_0}$ represents the relative lowering of the vapor pressure in a solution

containing one mol of solute to 100 mols of solvent. We then have $\frac{n}{N + n} =$

$\frac{p_0 - p_1}{p_0}$ the ideal solution equation which bears Raoult's name.

3. Raoult never accepted this as valid except for very dilute solutions. For all other solutions he continued to add a specific constant.

4. In spite of van't Hoff's demonstration to the contrary, Raoult continued to deal with the molecular weight of the solvent in the solution and not in the vapor. Even in 1890 Raoult did not understand the physical significance of the terms in the equation which bears his name.

The Determination of Volumes in Solution

The form of the osmotic pressure-vapor pressure equation here derived affords a new method of attack on an old problem that has drawn the attention of many workers. This problem is to determine the volume in the solution of the components of the solution. The process of solution is usually accompanied by some volume change so that the volume of the resulting solution is greater than, or less than, the sum of the volumes of the components before they were mixed. Only in the ideal solution as here defined will the volume of each component be the same after mixing as before. In every other case we must conclude that one or both components have expanded or contracted in the process of solution. The problem becomes of especial interest for a few

solutions which behave similarly to sodium hydroxide. "When four grams of sodium hydroxide are dissolved in ninety-six grams of water at 0° , the total volume is 0.6 cc. less than that of the original water."¹

It is rather improbable that the sodium hydroxide could have a negative volume of 0.6 cc. so that the determination of the specific volumes of the water and the sodium hydroxide becomes an interesting problem. This specific problem will not be solved here; but general methods for its attack will be outlined, and, in particular, a new one involving the use of Form I.

Cameron and Robinson² have given a good historical summary of the methods that have been used to solve this problem; but their assumption that all the volume change observed was due to the water seems somewhat improbable, and their condensation factors do not appear especially significant.

Among the earlier contributions to this problem was that of Gouy and Chaperon³ who, in studying the effects of gravity on change in concentration,

incidentally gave $K \frac{dw}{D_0}$ as the volume increase when dw grams of pure sol-

vent of density D_0 was added to unit volume of solution, K being a contraction or expansion coefficient characteristics of the solution. Since this coefficient must depend on concentration, it will be represented by X to show it is a variable. Gouy and Chaperon obtained as a value:

$$X = \frac{D_0}{D} \left(1 - \frac{dD}{dw} \right),$$

when D is the density of the solution. The volume of dw grams of solvent in the solution is $X \frac{dw}{D_0}$ and if dw equals one, the volume increase is V_x as defined in Form I. Consequently,

$$V_x = \frac{1}{D} \frac{(1 - dD)}{dw}.$$

Mr. Danforth Hale of this department has made a much simpler derivation of the same relation. We have:

$$D = \frac{M}{V}$$

in which D , M , and V , are the density, mass and volume of any solution. But M may be considered as made up of, the mass (m) of the solute which may remain constant, and the mass (w) of the solvent which is varied. Then

$$V D = m + w$$

differentiating

$$VdD + DdV = dw$$

and

$$\frac{dV}{dw} = \frac{1}{D} \left(1 - V \frac{dD}{dw} \right) = V_x$$

¹ Bousfield: Trans. Faraday Soc., 13, 141 (1917)

² J. Phys. Chem., 14, 1, 569 (1914).

³ Ann. Chim. Phys., (6) 12, 384 (1887).

This is seen to be equivalent to the expression of Gouy and Chaperon since they considered unit volume.

Teed¹ has calculated the value of the volume change coefficient by considering as simultaneous equations:

$$A a + B b = 100$$

$$A' a + B' b = 100$$

in which A and B are two original volumes of pure components which on mixing give one hundred volumes of solution, A' and B' are two slightly differing volumes also giving one hundred volumes of solution; and a and b are volume-change coefficients which are assumed to be constant over the narrow concentration range in question.

Unfortunately, the method is not correct, because a and b are not constants. If one takes the extreme case where a = 1 and solves for the volume change coefficient, one is really assuming that b is constant. For the present, all one can do is to attribute the whole change of volume to A and then to B, thus getting two volumes between which the true volume probably lies.

It has been suggested by Bancroft that the whole question of the determination of volumes of the components in a solution may be solved by the use of Form I to solve for V_s in those solutions for which the data are available. The usual plan has been to calculate V_s by various methods and then to calculate the osmotic pressure. This was the method of Berkeley, Hartley, and Burton² who applied a simplification of Porter's expression to the data for some sugar solutions. Their form was

$$P\bar{s} = RT \ln \frac{P_0}{P_1}$$

in which \bar{s} is our own V_s and was calculated from considerations similar to those just advanced for the volume change on solution together with reference to the compressibilities. Neither in Porter's own paper nor in Berkeley's does the molecular weight of the solvent vapor appear. The reason for this is not known; but this molecular weight must be introduced if one calculates the osmotic pressures as calculated by Berkeley. In Table IV the four more concentrated solutions are calculated from Berkeley; data for the two more dilute solutions coming from a different source as described below.

TABLE IV

| C | $\ln \frac{P_0}{P_1}$ | \bar{s} | P calc. | P obs. | V_s calc. | Sugar Density |
|--------|-----------------------|-----------|------------|-----------|----------------|------------------|
| 20.52 | .01144 | --- | --- | 14.38 | .9893 | 1.520 |
| 34.20 | .01950 | --- | --- | 24.82 | .9840 | 1.457 |
| 56.50 | .03580 | .99515 | 43.91 | 43.84 | .9974 | 1.624 |
| 81.20 | .05380 | .99157 | 67.43 | 67.68 | .9886 | 1.592 |
| 112.00 | .07983 | .98690 | 100.53 | 100.43 | .9885 | 1.594 |
| 141.00 | .10669 | .98321 | 134.86 | 134.71 | .9849 | 1.588 |

¹ "Volume Change on and in Solution" (1926).

² Phil. Trans., 218A, 295 (1919).

In Table IV, the first column shows the concentration of the solutions in grams of sucrose per 100 grams of water; the second column gives the natural logarithm of the ratio of the vapor pressure of pure water to the vapor pressure of the solution. In the third column are shown the values of \bar{s} (our own V_s) calculated by Berkeley from compressibility data and from considerations analogous to those advanced by Bancroft. These values of \bar{s} and $\ln \frac{p_0}{p_1}$ when substituted in his equation

$$P_s = RT \ln \frac{p_0}{p_1}$$

gave him his osmotic pressures in atmospheres shown in column four which are found to be quite close to the actual osmotic pressure observed for those solutions shown in the fifth column.

The method of Bancroft is exactly the opposite to that of Berkeley. The new method consists in substituting the values observed for P and $\ln \frac{p_0}{p_1}$ and from them, calculating V_s by means of the equation

$$V_s = \frac{RT}{PM_s} \ln \frac{p_0}{p_1},$$

which is Form I as here derived and in which V_s is the volume of one gram of the solvent *in the solution*. The sixth column shows the values of V_s that have been so calculated and it is emphasized that these values are as exact as the osmotic pressures and vapor pressures which were very carefully measured.

It will be observed from the Table that the values of V_s thus calculated differ from the \bar{s} values of Berkeley by less than 0.3%. This agreement may be interpreted to mean that the various refinements introduced into Berkeley's calculations were nearly correct, and achieved practically the same result as this new, more direct, and accurate method. Berkeley also gives data on $\ln \frac{p_0}{p_1}$ and \bar{s} for three other solutions whose concentrations are all greater

than 179 grams of sugar per 100 grams of water. Since this is the value usually given for the solubility of sucrose in water at 0°C., one wonders how these values were observed. No osmotic pressures are given for these last solutions.

Before describing the source of the data for the first two solutions in Table IV, the meaning of the last column may be explained. If we know the densities of the sugar solutions, we can calculate the volume of a definite weight of the solution. Then, if by such calculations as have just been given for V_s , we can determine the volume in the solution of one gram of water, multiplying this by the weight of water in the solution gives the volume occupied by the water. Subtraction of this volume from the volume of the solution gives the volume occupied by the sugar in the solution. Knowing the weight of the sugar and its apparent volume, we can calculate the apparent density of the sugar in the solution. These values as calculated for the solutions in ques-

tions are shown in the last column of Table IV. If, as is commonly held, in the process of solution, a solid undergoes a volume change comparable with its volume change on fusion, we should expect the densities of sugar in solution to be less than 1.588, its density as a solid. With this view, the data of the first two solutions are in better qualitative agreement. Also they agree better with the calculations of Teed. It is observed in both sets that the apparent density of the sugar decreases with increase in concentration. Much more work may well be spent on this point. In this calculation the tacit assumption has been made that each gram. of water occupies the same volume as every other gram of water.

In addition to the data from Berkeley, two other calculations were made for more dilute solutions. The results of these calculations are shown in the first two lines of Table IV. The osmotic pressures were taken from the measurements by Morse and the vapor pressures of sugar solutions of as nearly as possible the same concentrations were given by Dieterici.

Morse gives the osmotic pressure of a solution containing 20.52 grams of sucrose per 100 grams of water as 14.381 atmospheres. Dieterici reports the lowering of the vapor pressures of a solution of 20.66 grams sucrose per 100 grams of water as 0.052 mm. of mercury. Then $p_0 = 4.569$ and $p_1 = 4.517$

and $V_g = \frac{RT}{PM_2} \ln \frac{p_0}{p_1}$ then becomes:

$$V_g = \frac{0.08207 \times 273}{14.381 \times 0.018016} \ln \frac{4.569}{4.517}$$

from which $V_g = 0.9893$ cc.

Again, Morse gives as the osmotic pressure of a solution containing 34.20 grams sucrose per 100 grams of water 24.825 atmospheres and Dieterici gives the lowering of the vapor pressure by a solution containing 34.25 grams sucrose per 100 grams of water as 0.089 mm. of mercury. From these data $V_g = 0.9840$. These last two sets of data are those shown first in Table IV.

Table IV shows that these values of V_g are self-consistent but that they do not agree with those calculated from Berkeley's data. In both cases, with rising sugar concentration, the value of V_g decreases. The two sets of synthesized data are for more dilute solutions than those of Berkeley's solution containing 56.5 grams of sugar per 100 grams of water and they presumably should be greater.

It may be added that the values of V_g for the two more dilute solutions fall practically on the curve plotted from the densities of sugar solutions while those calculated from the data of Berkeley are decidedly different. In Berkeley's table summarizing the experiments, \bar{s} for the solution containing 81.2 grams of sugar is given as 0.99157, but in the Table first recording the values of \bar{s} as calculated from the density and compressibility data, the value is given as 0.98157. This however would have no effect on the present calculation of V_g . In a note at the end of the paper is given a corrected value for $\ln (p_0/p_1)$ for this solution as 0.5239. This is a rather large correction and makes the calculated V_g become 0.9685 which is apparently much too low.

It has been found that except for this solution the values of V_x calculated by the method of Baneroff agree within 0.2% except for this concentration in question. The conclusion is drawn that either some abnormal effect enters at about that concentration, absent above or below it, or that the osmotic pressure for that concentration is less accurate than the rest.

Application of van der Waals' Formula to Osmotic Pressures

Soon after van't Hoff derived the relationship between osmotic pressure and the gas pressure of the solute, it became evident that the convenient approximation $PV = RT$ suggested by van't Hoff could not express the facts of osmotic pressure for solutions of finite concentrations any more than $PV = RT$ expresses the relation for a gas over the whole range. As indicated above, van't Hoff knew that this would be true and early stated that these deviations appeared in the two cases for the same reason.

Naturally, the first method of attack was to test the applicability of van der Waals' equation which was known to express the behavior of gases. Numerous workers have made efforts to express osmotic pressures by equa-

tions having a form similar to van der Waals' equation $(P + \frac{a}{V^2})(V - b) = RT$

in which, for gases, V is the volume occupied by the gas, $\frac{a}{V^2}$ is a term correcting

for the mutual attraction of the gas molecules and b is a term correcting for the volume occupied by the gas molecules themselves. In the applications of this type of formula to actual data, it has been found that the data for osmotic pressures may be represented fairly well by $P(V - b) = RT$. One of the earliest of these applications was made by A. A. Noyes¹ who calculated osmotic pressures from the freezing-points of Beckmann. These osmotic pressures were then found to fit rather closely into a complicated formula which might be simplified into $P(V - d) = K$. Seven years later Noyes and Abbot² reported work done on some ethereal solutions of which they measured the vapor pressures. By means of a formula newly developed, which simplifies into our Form I, they calculated the osmotic pressures of these solutions, and found that $PV = RT$, where V equals volume of solution, fitted quite well over the range covered, 0.0 - 0.25 mols of nitrobenzene or naphthalene per liter.

Sackur³ also used freezing points to calculate osmotic pressure and found that $P(V - b) = RT$ was quite satisfactory. Although he was using the data of Morse and Frazer, he chose to represent by V the volume of solution, showing that thus the calculations came out better than by the use of volume of solvent which they had used. The difference between $V - b$ and V_1 will probably be rather small for the dilute solutions, so the advantage is not marked.

¹ Z. physik. Chem., 5, 53 (1890).

² Z. physik. Chem., 23, 56 (1897).

³ Z. physik. Chem., 70, 477 (1910).

Bousfield also used the data of Morse and Frazer to support his hydration theories. He derives the formula,

$$P(h - n) = R'T$$

where $h - n$ represents the amount of free water and R' is not the gas constant. By this use of such an equation he calculated that at 20°C., N , the hydration factor for sucrose comes out 6, and this factor diminishes with increase in temperature. Before leaving this matter, it might be well to point out that Frazer and Myrick¹ themselves were able to represent their own measurements of osmotic pressure by our Form I, up to 6.5 molar concentration and osmotic pressure of over 250 atmospheres.

It is, therefore, clear that the method offered in this section is not particularly new, but is decidedly more extensive than those previously published. If we assume that the solution studied is an ideal solution, we may then by,

$$PV_M = RT \ln \frac{N + n}{N},$$

or

$$PV_I = RT \frac{N}{n} \ln \frac{N + n}{N}$$

calculate the osmotic pressure for any concentration of solute from 0 to 100 percent, and may then introduce the values of osmotic pressure so found, into any convenient formula.

That such ideal solutions actually exist has been shown by Zawidzki² who carried out distillations and then from the composition of the distillate calculated the partial pressure of each component in the vapor over the original solution. If the solutions are ideal, their partial pressures plotted against the liquid composition should be straight lines and this was found to be true for seven pairs of solutions: benzene-chlorobenzene; benzene-bromobenzene; benzene-ethylene chloride; toluene-chlorobenzene; toluene-bromobenzene; ethylene bromide-propylene bromide; and methylchloride-carbon dioxide. It was not true for many other pairs in nearly all of which at least one component was known to be associated.

Rosanoff and Easley³, working probably a bit more accurately, confirm this relation for benzene-ethylene chloride which is the only one of Zawidzki's solutions used by them. Ten years later, Schulze⁴ reported some calculations on the vapor pressures of benzene-toluene solutions which at the lower temperatures he interprets to indicate polymerization of the toluene. At 60°C. however, the total pressure over such a solution plotted against composition of the liquid is a straight line. Since this is a requirement for an ideal solution, we may conclude that, at least at 60°, benzene and toluene form an ideal solution within the limits of error of vapor pressure measurements.

¹ J. Am. Chem. Soc., 38, 1915 (1916).

² Z. physik. Chem., 35, 129 (1900).

³ J. Am. Chem. Soc., 31, 953 (1909).

⁴ Ann. Physik, (4) 59, 73 (1919).

In the calculations of this section, we shall assume that at 27°C benzene and toluene form an ideal solution. Whether they do or not is immaterial since they are selected merely for the sake of concreteness. Hypothetical liquids A and B, having assigned hypothetical densities, vapor pressures, and molecular weights might have been used; but the following calculations are based on an idealized benzene and an idealized toluene.

In the first column of Table V are shown the mol fractions of benzene in each solution; from this the mol fraction of the toluene can be obtained by difference. In the second column are given the osmotic pressures of benzene, calculated at 300° abs. from either Form III or Form IV, equations for the ideal solution; while the osmotic pressures of the toluene are shown in the third column.

TABLE V

Formula applied: $(P + a/V^2)(V - b) = RT$ where P is the osmotic pressure and V is the volume of the solution containing one gram molecular weight of the solute.

Temperature 300° abs.

For benzene as solute, $b = 0.60$, $a = .79198$,

For toluene as solute, $b = .081$, $a = .8338$,

Mol volumes: benzene = .09006; toluene = .10772.

| Mol Fraction Benzene $\frac{n}{n+N}$ | Osmotic pressure | | Volume of solution containing one mol of solute | | R calculated | |
|-----------------------------------------------|----------------------------------------|----------------------------------------|-------------------------------------------------------|-----------------------------|-------------------------|-------------------------|
| | Benzene as Solute Atmospheres | Toluene as Solute Atmospheres | Benzene Solute Liters | Toluene Solute Liters | Benzene as Solute | Toluene as Solute |
| .99 | 1051.7 | 2.74 | .09115 | 9.0237 | (.1191) | .0820 |
| .95 | 684.15 | 14.01 | .09573 | 1.8189 | (.0917) | .0826 |
| .9 | 525.83 | 28.75 | .10203 | .91826 | .0843 | .0830 |
| .8 | 367.55 | 60.95 | .11699 | .46796 | .0806 | .0835 |
| .7 | 275.00 | 97.51 | .13622 | .31786 | .0807 | .0835 |
| .6 | 209.26 | 139.43 | .16187 | .24281 | .0813 | .0828 |
| .5 | 158.30 | 189.34 | .19778 | .19778 | .0820 | .0820 |
| .4 | 116.66 | 250.30 | .25164 | .16776 | .0824 | .0810 |
| .3 | 81.52 | 328.97 | .34141 | .14632 | .0828 | .0801 |
| .2 | 50.96 | 439.63 | .52094 | .13023 | .0827 | .0802 |
| .1 | 24.04 | 628.99 | 1.05954 | .11773 | .0824 | .0838 |
| .05 | 11.71 | 818.3 | 2.1376 | .11246 | .0822 | (.0927) |
| .01 | 2.29 | 1257.9 | 10.7544 | .10862 | .0820 | (.1223) |
| Mean..... | | | | | .0821 | .0822 |

Since the volume V_1 in the more concentrated solutions is smaller¹ than any volume into which the liquid solute can be compressed, it seemed desirable to establish a relation between osmotic pressures and the volume, V, in liters, of the solution in which one gram molecular weight of the solute is dis-

¹ Bancroft: J. Phys. Chem., 10, 320 (1906).

solved. It will be evident that the volume V , of the solution containing one mol of solute is equal to the sum of the volume of the solvent V_1 in which one mol of the solute is dissolved and the volume (M.V.) of one mol of the solute.

$$\text{Or } V = V_1 + (\text{M.V.}) \text{ solute}$$

It should be emphasized that in doing this, we are in no way detracting from the increased applicability of $PV_1 = RT$ over $PV = RT$ for dilute solutions. Neither of these formulas is valid beyond very dilute solutions while the use of V as volume of solution in an equation exactly of the van der Waals' form,

$$(P + a/V^2)(V - b) = RT$$

expresses the osmotic pressure of either component with a deviation of less than 2% up to and including a solution containing nine mols of solute to one mol of solvent.

The fourth and fifth columns show the values of V introduced into the van der Waals equation. In calculating the osmotic pressures, the value of R was taken as 0.0820 liter atmospheres per degree instead of 0.08207. Consequently R should equal 0.0820 from the van der Waals equation and the values actually calculated are shown in columns six and seven.

The equation, then, reproduces the data satisfactorily over the range of mol fraction of solute, 0 to 0.9 though nothing short of absolute agreement can be considered really satisfactory for idealized data. By putting in more terms in the equation of state, we can of course get a better agreement. If we write

$$(P + a/V^2)(V - b - c/V^n) = RT$$

it is possible to represent the facts pretty well over the entire range of mol fractions 0 to 0.99, as is shown in Table VI).

TABLE VI

Formula applied: $(P + a/V^2)(V - b - c/V^n) = RT$

Temperature 300° abs.

For benzene as solute, $c = 2.69 \times 10^{-22}$, $n = 18.8$,

For toluene as solute, $c = 8.45 \times 10^{-22}$, $n = 27$.

| Mol Fraction Benzene | R Benzene as Solute | R Toluene as Solute | Mol Fraction Benzene | R Benzene as Solute | R Toluene as Solute |
|----------------------|---------------------|---------------------|----------------------|---------------------|---------------------|
| .99 | .0820 | .0820 | .4 | .0824 | .0810 |
| .95 | .0819 | .0826 | .3 | .0828 | .0801 |
| .90 | .0820 | .0830 | .2 | .0827 | .0801 |
| .8 | .0805 | .0835 | .1 | .0824 | .0820 |
| .7 | .0807 | .0835 | .05 | .0822 | .0823 |
| .6 | .0813 | .0828 | .01 | .0820 | .0820 |
| .5 | .0820 | .0820 | Mean | .0819 | .0820 |

These values of b so found to fit into the van der Waals equation appear to have real significance. In the first place, they are specific, for if values be introduced differing markedly from them, no value of a can be found that will make the value of R remain so nearly constant as do these accepted values.

In the second place these values appear to represent a fundamental quantity for each solute. In the case of benzene, b is 67% of the mol volume of the liquid; for toluene, the fraction is 75.3%. Similar calculations have been made with similar results for the system benzene-carbon tetrachloride. Again $b = .060$ is the value best fitting for benzene and b for carbon tetrachloride is 0.073 which is again 75% of the mol volume of the liquid carbon tetrachloride at that temperature.

The suggestion is made that these values of b may represent the actual volume of these molecules at this temperature, or, since the data are idealized, that the volume of the molecules of liquids having these densities represents this fraction of the molecular volume of the liquids. Numerous authors have shown by various methods that the b of van der Waals' equation cannot be independent of temperature and pressure so that it should not be expected that the values here used should be those values of b which are suitable for benzene as a gas at elevated temperatures. The proposed value is about one half the latter. But measurements on liquids ought to lead to this sort of fraction and they do. Tammann,¹ from measurements of compressibility of liquids at 0°, calculated for a few liquids that the volume when the pressure is infinite averages 0.718 times the volume of the liquid at 0°. Korber extended these studies on compressibilities and made some on thermal expansion for a number of liquids. These give average values for $V_{t=0^{\circ}\text{abs.}} = 0.756$ and $V_{p=\infty} = 0.72$. It is clear then, that the values of b thus satisfying van der Waals' equation as here applied have quite closely the same magnitude as these "incompressible" volumes of other methods.

Conclusions

1. Two equivalent expressions for the relation between osmotic pressures and vapor pressures have been derived in a manner analogous to that of van't Hoff. These expressions are:

$$PV_g = \frac{RT}{M_2} \ln \frac{p_0}{p_1}$$

or

$$PV_M = RT \ln \frac{p_0}{p_1}$$

and

$$PV_1 = RT \frac{N}{n} \ln \frac{p_0}{p_1}$$

2. No equation of the form $PV = RT$ can express osmotic pressures accurately. If V be defined as the volume V_1 of the solvent containing one mol of solute, the data of Morse and Frazer showed the applicability of $PV_1 = RT$ to be greater than that of $PV = RT$ where V is the volume of solution.

¹ Ann. Physik, (4) 37, 975, 1014 (1912).

3. The heat of dilution corresponds to a work term which prevents any form of $PV = RT$ having validity over a range of concentration. The equation must be $PV = RT + f(Q)$ where $f(Q)$ is a function that cannot be evaluated at present.

4. For ideal solutions we can write $PV_I = RT$ with an error not to exceed five percent to the concentration where the solute is ten mol percent of the solution.

5. From Form II, $PV_I = RT \frac{N}{n} \ln \frac{p_0}{p_1}$, in so far as $PV_I = RT$ may be assumed to be valid, $\frac{n}{N} = \ln \frac{p_0}{p_1}$ is a general equation for the calculation of molecular weights.

6. This equation $\frac{n}{N} = \ln \frac{p_0}{p_1}$ is important because from the Clausius-Clapeyron equation $\ln \frac{p_0}{p_1} = \frac{Q}{RT^2} dT$. Substituting in this and simplifying, we get $M = \frac{Kg}{\Delta T}$ which is the equation for the calculation of molecular weights from freezing points or boiling points.

7. Raoult's law and Henry's law are shown to be essentially different, because the constant in Raoult's law is non-specific and the one in Henry's law is specific. Also because the term p_0 , the vapor pressure of the pure liquid, has no physical significance in the case of a gas above its critical temperature.

8. From the equation $PV = RT \left(\frac{N}{n} + \frac{(M.V.)_1}{(M.V.)_2} \right) \ln \frac{p_0}{p_1}$, an equation which is just as valid as Form II, in so far as $PV = RT$,

$$\frac{n}{N + \frac{(M.V.)_1}{(M.V.)_2} n} = \frac{p_0 - p_1}{p_0}$$

is obtained of the general form of Raoult's law. This may not be significant, because Raoult's law holds accurately for benzene-toluene mixtures at temperatures at which the two molecular volumes are not equal.

9. Objections to van't Hoff's relation on the ground of inadequacy have often rested upon improper definitions of the terms, especially the V of $PV = RT$.

10. Compressibility of the solvent is not a factor in measurements of osmotic pressure.

11. Some previous methods of finding the volumes of the components of a solution in the solution are discussed and it is shown that the volume of one gram of solvent in a solution may be calculated from Form I, using it as $V_s = \frac{RT}{PM_2} \ln \frac{p_0}{p_1}$. This permits the calculation of the specific volume of the solvent.

12. It has been shown that V_s for either component can be determined from the density relations, subject to a correction for possible hydrates of

varying composition. This correction is probably of slight importance when one calculates V_g for moderately concentrated solutions. Subject to this limitation, it is possible to calculate osmotic pressures accurately from a knowledge of the densities and the partial pressures.

13. The osmotic pressures of ideal solutions of benzene and toluene are calculated from either form here derived.

14. These osmotic pressures are shown to be expressed quite satisfactorily by an equation $(P + a/V^2)(V - b) = RT$ which is of the type used by van der Waals for gases.

15. The absolute validity of Raoult's law for ideal solutions gives rise to some very interesting problems in regard to mass and volume concentrations. These will be discussed in detail in a later paper.

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AQUEOUS SOLUTIONS OF SODIUM SILICATES.* PART VIII.
GENERAL SUMMARY AND THEORY OF CONSTITUTION.
SODIUM SILICATES AS COLLOIDAL ELECTROLYTES.

BY R. W. HARMAN

Introduction

The interest of recent years in the ever-increasing industrial importance of sodium silicates of varying ratios $\text{Na}_2\text{O}:\text{SiO}_2$, as evidenced by their many and varied technical applications and their increased production, seems to have overshadowed the more theoretical aspect of their exact nature and behaviour in solution, from a knowledge of which we can, alone, hope to understand fully and apply more widely still this class of exceedingly puzzling but useful compound.

Although silicates generally have been subjected to extensive and prolonged investigations, sodium silicates, in particular, have received only isolated and intermittent attention. Until quite recently our knowledge of aqueous solutions of the alkali silicates was drawn mainly from the work of Kohlrausch¹, and from Kahlenberg and Lincoln,² on the electrical conductivity and from the work of Kahlenberg and Lincoln, and Loomis³ on freezing point lowering. These investigators concluded that alkali silicates are largely hydrolysed in solution, most of the silica being in the colloidal state. Later Bogue⁴ showed that the degree of hydrolysis as determined by E.M.F. measurements was unexpectedly low and not in accord with the previous conclusions drawn from measurements of conductivity and lowering of the freezing point.

The literature contains many references to several definite sodium silicates, notably Na_2SiO_3 , $\text{Na}_2\text{Si}_2\text{O}_6$, NaHSiO_3 , $\text{Na}_2\text{Si}_5\text{O}_{11}$, Na_4SiO_4 , etc. but the only one whose composition had been definitely established was the metasilicate, Na_2SiO_3 , and even then much conflicting data existed concerning the number of its hydrates. Then Morey⁵, Morey and Brown⁶ proved that Na_2SiO_3 and $\text{Na}_2\text{Si}_2\text{O}_6$ separated as crystalline salts at temperatures between $400^\circ\text{--}1000^\circ\text{C}$ from solution and from fused melts. The existence of the other sodium silicates seems more or less to have been taken for granted, as being probably formed from the great array of silicic acids postulated

*This series of papers, "Aqueous Solutions of Sodium Silicates Parts I-VIII, comprise a Thesis presented for the Degree of Doctor of Science of the University of London.

¹ Wied. Ann., 47, 756 (1892); Z. physik. Chem., 12, 773 (1893).

² J. Phys. Chem., 2, 77 (1898).

³ Wied. ann., 60, 531 (1897).

⁴ J. Am. Chem. Soc., 42, 2575 (1920).

⁵ J. Am. Chem. Soc., 36, 215 (1914).

⁶ J. Phys. Chem., 28, 1167 (1924).

from time to time, e. g. Schwarz and Menner¹ claim the existence of at least seven silicic acids, or hydrates of SiO_2 . Our knowledge of these is, at best, very meagre and their existence as acids seems very problematical, even the mostly clearly defined of all, metasilicic acid, H_2SiO_3 , on account of its partly colloidal nature, being still wrapped in an atmosphere of mystery.

General Summary of Experimental Work and Results

In the present investigation the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ at 25°C has been studied along the following lines, each of which has formed the subject of a communication to this journal,—(1) preparation and conductivity, (2) transport numbers, (3) sodium ion activity, (4) hydrolysis (5) osmotic activity: lowering of F.Pt. and v.p., (6) heterogeneous equilibria (7) electrometric titration, diffusion, and colorimetric estimation of silicate.

A brief summary of the results obtained and the more important conclusions therefrom, follow *seriatim*.

(1) Conductivity.

From measurements of aqueous solutions of ratios 2:1, 1:1, etc. up to 1:4 we have seen² that solutions of 2:1 and 1:1 ratios are excellent conductors in dilute solution but the equivalent conductivity falls quickly with increase of concentration, so that at $2N_w$ it is relatively low. The ratios containing more silica, viz., 1:2, 1:3, and 1:4 are also quite good conductors in dilute solution and moreover the values of Δ_∞ for these three ratios are all nearly equal, being 95, 91 and 88, but in concentrated solution the conductivities are abnormally low.

Hydrolysis into NaOH and colloidal silicic acid cannot account for this high conductivity, not even with ratios relatively rich in NaOH , nor in dilute solution where hydrolysis is greatest; and with ratios rich in silica, where hydrolysis is practically negligible, it is apparent that the explanation that the conductivity is due to hydrolysis is totally inadequate.

The results obtained are reproduced again in Table I for ready reference.

| N_w | Equivalent Conductivity | | | | $t = 25^\circ\text{C}$. | | |
|-------|-------------------------|--------|--------|--------|--------------------------|-------|-------|
| | NaOH | 2:1 | 1:1 | 1:1.5 | 1:2 | 1:3 | 1:4 |
| 2.0 | 142.0 | 57.32 | 57.25 | 32.09 | 25.80 | 20.46 | 16.17 |
| 1.0 | 172.50 | 85.57 | 81.25 | 50.23 | 36.10 | 31.42 | 23.24 |
| 0.5 | 200.0 | 107.80 | 96.80 | 66.76 | 49.05 | 45.41 | 33.14 |
| 0.2 | 209.0 | 136.90 | 112.70 | 86.20 | 62.59 | 57.33 | 48.25 |
| 0.1 | 214.5 | 157.50 | 130.80 | 99.20 | 72.70 | 66.48 | 57.80 |
| 0.05 | 220.0 | 175.50 | 143.80 | 107.04 | 78.00 | 75.63 | 65.80 |
| 0.02 | 225.5 | 190.10 | 152.70 | 114.20 | 84.00 | 81.75 | 75.06 |
| 0.01 | 227.5 | 193.0 | 155.0 | 118.10 | 89.50 | 85.16 | 81.50 |
| 0.005 | 228.0 | 194.2 | 159.0 | 120.14 | 93.20 | 89.90 | 86.04 |
| 0.0 | | | 160.0 | 121.00 | 95.00 | 91.00 | 88.00 |

¹ Ber., 57 B, 1477 (1924); 58 B, 73 (1925).

² J. Phys. Chem., 29, 1155 (1925).

The most reasonable assumption to explain these results is the existence of silicate ions and sodium ions due to ionisation, in addition to the NaOH formed by hydrolysis. In concentrated solution this ionisation falls off considerably or else the silicate ions are now not so active in conveying the current.

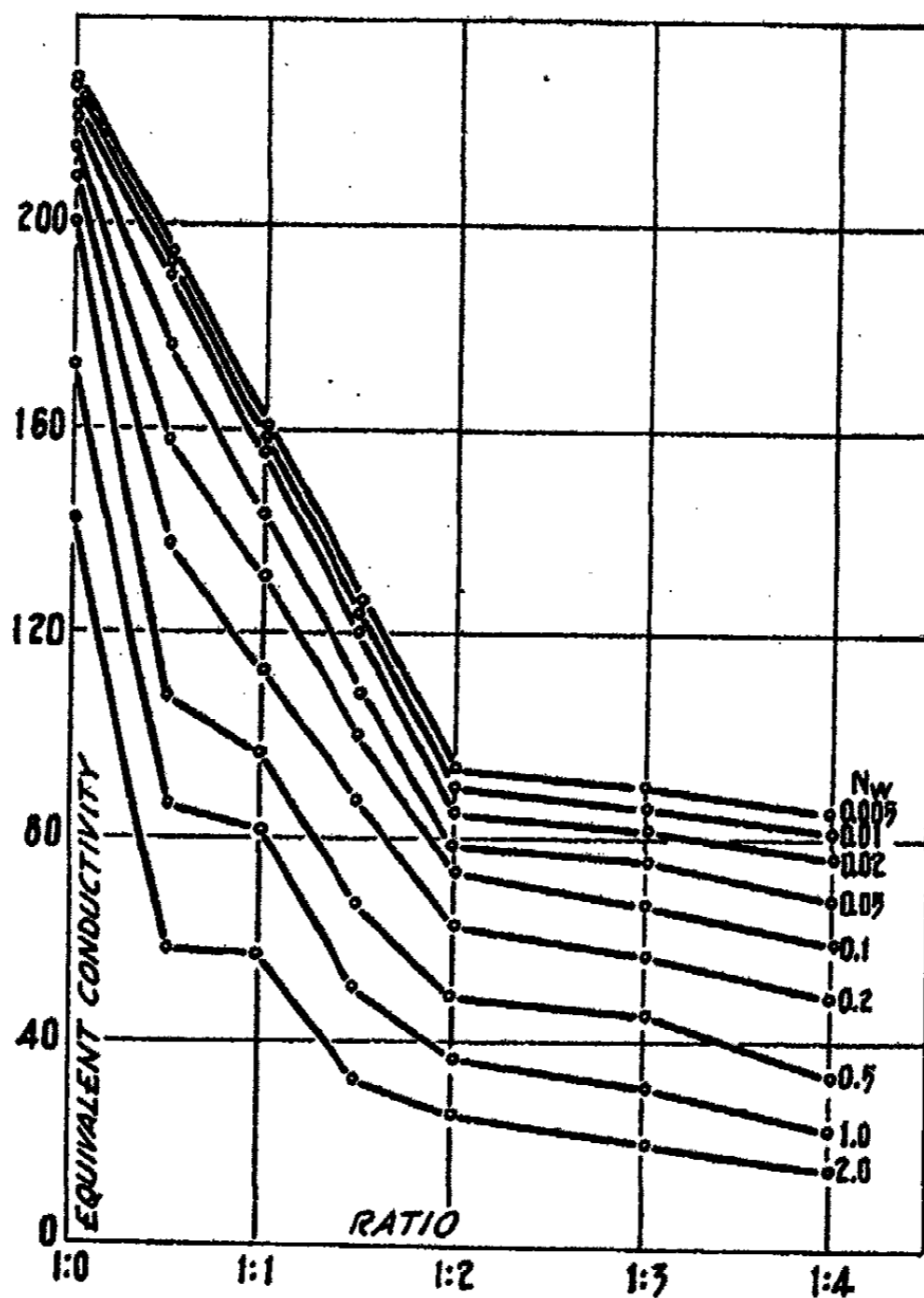


FIG. 1
Equivalent Conductivity against Ratio

From the graph where the equivalent conductivity is plotted against the ratio, as in Fig. 1, we have seen that in dilute solution there is a sharp change of direction at 1:2, the relationship on either side of this point being linear. As the solutions become more concentrated this simple relationship disappears until at $2 N_w$ the most marked changes of direction of the curves are evident at 2:1 and 1:1. It may be that definite salts of ratios 2:1, 1:1 and 1:2 exist, but in any case, concentrated solutions exhibit a radically different behaviour from very dilute solutions, suggestive of a change of state of one or more of the constituents.

(2) *Transport Numbers.*

From the results of very careful transport number experiments¹ we have seen that as the proportion of SiO_2 increases in the ratio $\text{Na}_2\text{O}:\text{SiO}_2$ so does the proportion of the current carried by the silica constituent increase. If the transport numbers are calculated on the assumption of SiO_3^{2-} being present in all ratios, then the T.N. of this silicate ion is as shown in Table II.

From this it is fairly evident that (1) silicate ions are present and (2) that either (a) the anion may be a solvated aggregate of simple SiO_3 ions, carrying a charge equal to the sum of the total charges on the separate ions, or a solvated aggregate containing more than one mol SiO_2 per divalent charge,

TABLE II
T.N. Silicate = $\frac{\text{total change in wt. of SiO}_2 \text{ content}}{\text{wt. SiO}_2 \text{ equiv. to Ag deposited in coulometer.}}$

| No. Expt. | Ratio | Approx. Nw. | t_{Na} | t_{SiO_2} | t_{OH} |
|-----------|-------|-------------|-----------------|--------------------|-----------------|
| 1 | | 2.36 | 0.27 | 0.17 | 0.56 |
| 2 | 1:1 | 1.0 | 0.36 | 0.13 | 0.51 |
| 3 | | 0.1 | 0.31 | 0.18 | 0.51 |
| | | | Mean 0.31 | 0.16 | 0.53 |
| 4 | | 1.0 | 0.42 | 0.88 | |
| 5 | 1:2 | 0.5 | 0.35 | 0.70 | |
| 6 | | 0.1 | 0.45 | 0.87 | |
| | | | Mean 0.41 | 0.82 | |
| 7 | 1:3 | 1.0 | 0.40 | 1.35 | |
| 8 | | 0.5 | 0.45 | 1.42 | |
| | | | Mean 0.43 | 1.38 | |
| 9 | 1:4 | 1.0 | 0.53 | 2.32 | |
| 10 | | 0.1 | 0.44 | 2.44 | |
| | | | Mean 0.48 | 2.38 | |

these aggregates splitting up on dilution, or (b) the anions may be definite ions more complex than the simple ion SiO_3 ion, i.e. definite salts of the following formulae may exist, $\text{Na}_2(\text{SiO}_3 \cdot \text{SiO}_2)$, $\text{Na}_2(\text{SiO}_3 \cdot 2\text{SiO}_2)$ etc., which ionise to give definite divalent silicate ions such as, $(\text{SiO}_3 \cdot \text{SiO}_2)^{2-}$, $(\text{SiO}_3 \cdot 2\text{SiO}_2)^{2-}$, etc.

In this paper on transport numbers it was pointed out that the number of mols of SiO_2 per divalent charge (2 F) of the silicate anion seemed approximately equal to the molar ratio $\text{SiO}_2 : \text{Na}_2\text{O}$. This may be explained in two ways,—(1) ratio 1:4 e.g. may be a definite salt with a true anion of the composition $(\text{SiO}_3 \cdot 3\text{SiO}_2) \text{ aq.}^{2-}$ i.e. such an anion results at any and all concentrations from ionisation, or (2) in solutions of ratio 1:4 an aggregate such as $(\text{SiO}_3 \cdot n\text{SiO}_2) \text{ aq.}^{2-}$ exists in a more loosely bound combination, in such a way

¹ J. Phys. Chem., 30, 359 (1926).

that "n" may be large in very concentrated solutions, but in very dilute solutions smaller and even zero, though in the range of concentration measured, as far as experimental conditions allow, it appears on an average equal to four. In such circumstances it was concluded not to be so misleading to calculate the T. N. of the silicate anion from

$$\text{T. N. Silicate} = \frac{\text{total change in wt. of SiO}_2 \text{ content}}{N \times (\text{wt. of SiO}_2 \text{ equiv. to Ag deposited in coul.})}$$

and the results obtained are given again in Table III.

TABLE III
Transport Numbers

| N | Ratio | t_{Na} | $t_{sil.}$ | t_{OH} |
|---|-------|----------|------------|----------|
| 1 | 1:1 | 0.37 | 0.16 | 0.53 |
| 2 | 1:2 | 0.41 | 0.41 | 0.18 |
| 3 | 1:3 | 0.43 | 0.46 | 0.11 |
| 4 | 1:4 | 0.48 | 0.59 | — |

(3) *Sodium Ion Activity.*

The measurements of sodium ion activity by means of a sodium amalgam electrode¹ were carried out in the hope of gaining some idea of the sodium ion concentration in solutions of these various ratios. The results with ratio 1:1 however, were anomalous in that the curve of γ , the activity coefficient, against concentration, passed through a minimum at moderate concentration, about $0.1N_w$, and so caused some irregularity, but the results obtained with the higher ratios did not show similar behaviour. The activity coefficient, from being comparatively high in dilute solution, changed regularly to a very low value in concentrated solution, being more or less parallel to the conductivity. The fall in γ as the proportion of SiO_2 in the ratio $\text{Na}_2\text{O} : \text{SiO}_2$ increased was also fairly regular.

TABLE IV
Sodium Ion Activity

| Conc. N_w . | $\gamma = \text{activity coefficient}$ | | | |
|---------------|----------------------------------------|-------|-------|-------|
| | 1:1 | 1:2 | 1:3 | 1:4 |
| 1.0 | | 0.265 | 0.105 | 0.050 |
| 0.80 | 0.475 | 0.275 | 0.145 | 0.060 |
| 0.50 | 0.440 | 0.310 | 0.185 | 0.090 |
| 0.40 | 0.425 | 0.335 | 0.210 | 0.110 |
| 0.20 | 0.415 | 0.410 | 0.295 | 0.185 |
| 0.10 | 0.425 | 0.460 | 0.365 | 0.250 |
| 0.05 | 0.500 | 0.500 | 0.425 | 0.325 |
| 0.025 | 0.700 | 0.525 | 0.480 | 0.405 |
| 0.01 | 0.975 | 0.785 | 0.700 | 0.550 |

¹ J. Phys. Chem., 30, 917 (1926).

The general conclusions can be drawn that increase of concentration for any one ratio, and especially increase of silica in the ratio, both have a very marked effect on the activity of the sodium ion, so reducing it that in concentrated solutions of ratios 1:3 and 1:4 it is remarkably and unexpectedly low. The results obtained are summarised in Table IV.

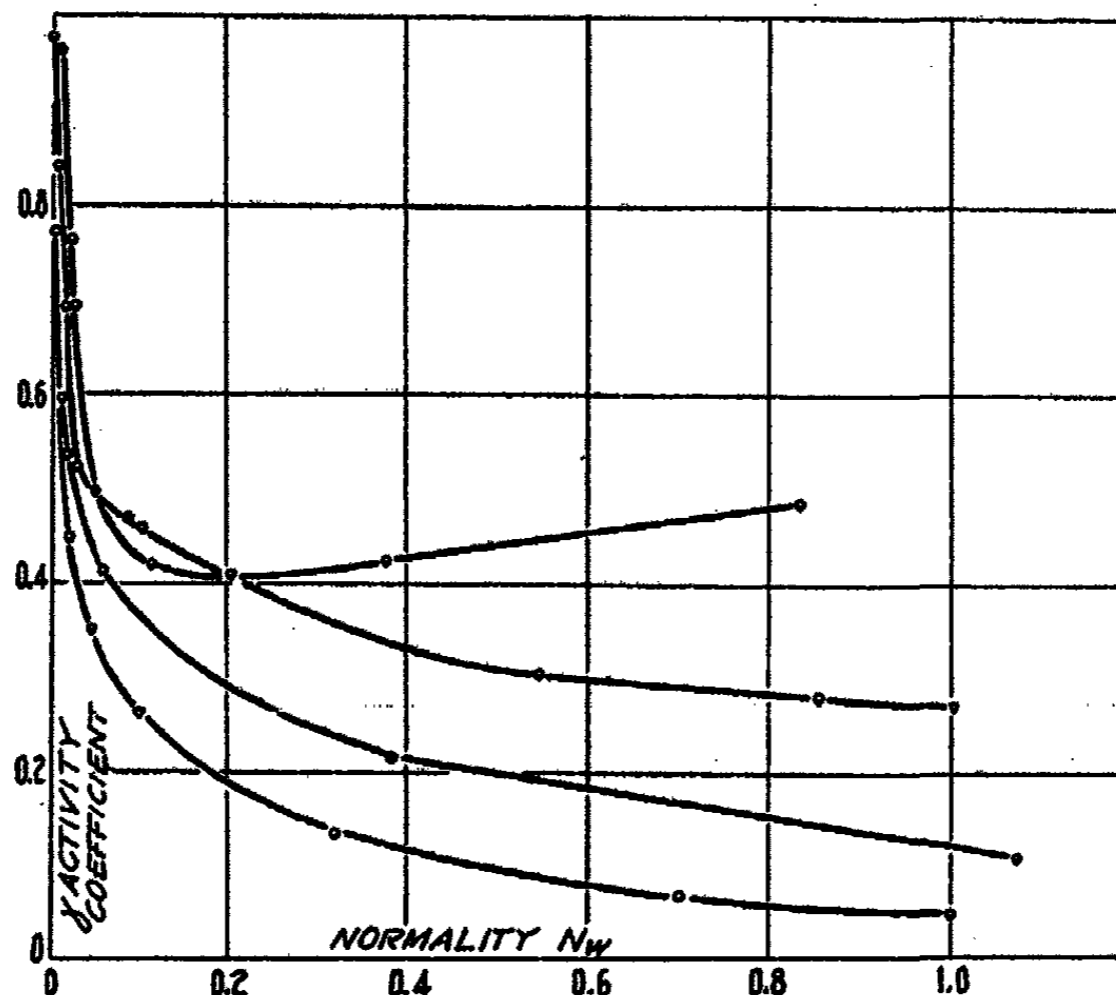


FIG. 2
Sodium Ion Activity, γ , against Concentration

These results are shown graphically in Fig. 2.

(4) *Hydrolysis.*

The description of E. M. F. measurements of hydrogen ion concentrations is given in Part IV of this series¹ the chief results of which are summarised in Table V.

TABLE V
Percentage Hydrolysis

| N _w | 2:1 | 1:1 | 1:1.5 | 1:2 | 1:3 | 1:4 |
|----------------|------|-------|-------|------|-------|-------|
| 2.0 | 17.5 | 15.25 | 3.0 | 1.0 | 0.101 | 0.032 |
| 1.0 | 19.0 | 16.5 | 5.9 | 1.35 | 0.192 | 0.071 |
| 0.5 | 19.7 | 19.1 | 7.10 | 1.88 | 0.36 | 0.14 |
| 0.2 | 24.2 | 20.0 | 8.25 | 2.40 | 0.58 | 0.35 |
| 0.1 | 28.4 | 21.8 | 8.7 | 2.85 | 0.77 | 0.57 |
| 0.05 | 31.6 | 22.6 | 9.76 | 3.8 | 1.10 | 0.93 |
| 0.02 | 34.2 | 23.25 | 11.0 | 5.1 | 1.20 | 1.30 |
| 0.01 | 36.0 | 27.8 | 12.0 | 6.5 | 1.34 | 1.50 |

¹ J. Phys. Chem., 30, 1100 (1926).

These results are shown graphically in Fig. 3.

It was there shown that the degree of hydrolysis and the concentration of OH ion are in a measure proportional to the proportion of Na_2O in the ratio. The great point of interest however, is that even in very dilute solution ratio 1:1 shows only 27.8% hydrolysis, while ratios 1:3 and 1:4 only about 1.5% hydrolysis. In concentrated solution the degree of hydrolysis is even more remarkably low, being 15% and 0.1 and 0.03% respectively for concentration

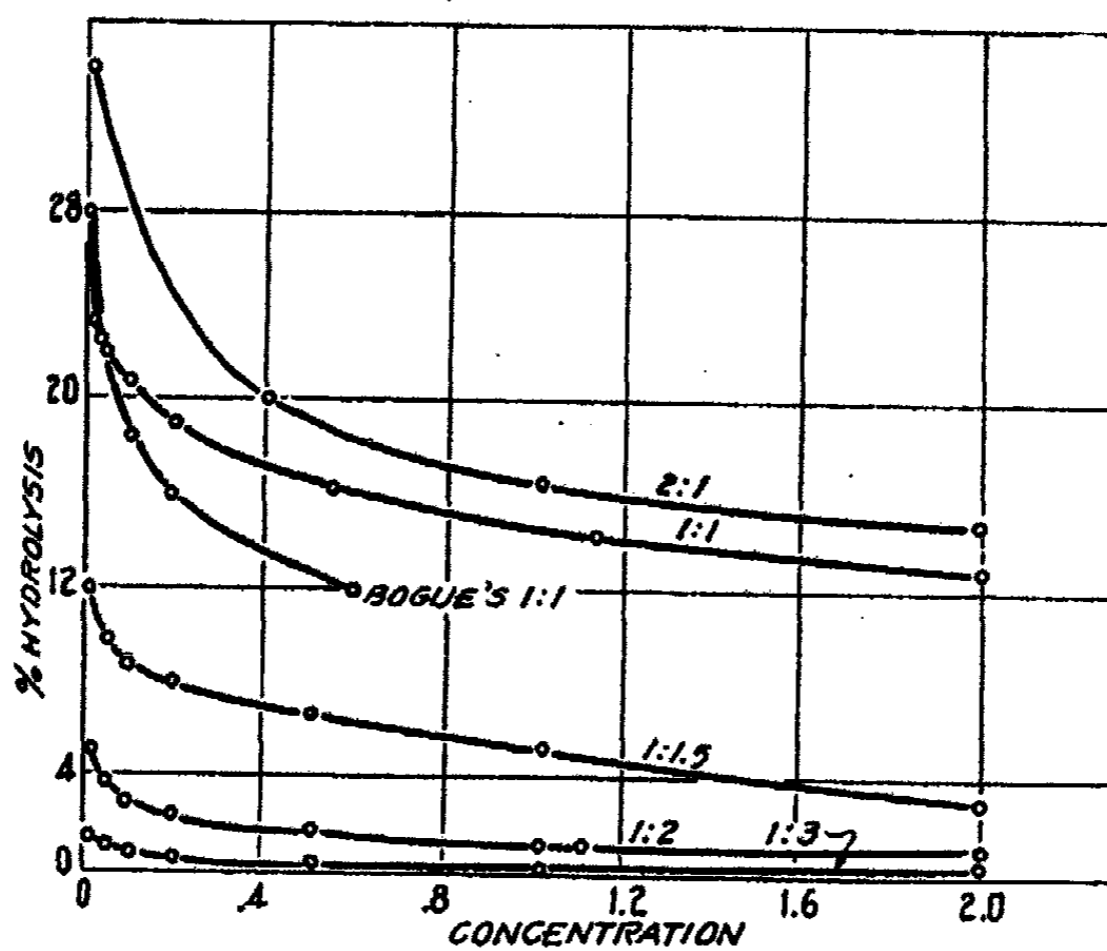


FIG. 3
Percentage Hydrolysis against Concentration

$2N_w$. We thus see that hydrolysis can in no way explain the conductivity of these silicate solutions. If, as some later investigators have assumed, the OH ion concentration, as here calculated from measurements by the hydrogen electrode, does not give the true value of the hydrolysis, then OH ion adsorption by the colloidal silica takes place to a very large extent, especially in the higher ratios. Hence these solutions should show a very low osmotic activity, which they do not, a point to be dealt with more fully later in considering results of measurements of F.Pt. lowering. The only other explanation seems to be that silica exists in the crystalloidal state in solution, some possibly as silicate ions, and is not wholly colloidal as heretofore supposed.

From Table I¹ (Part IV) giving the values of the liquid-liquid potential difference sodium silicate/sat. KCl, as experimentally determined by the Bjerrum extrapolation method, in ratios 2:1 and 1:1 this liquid-liquid P.D. is of the order of 3-4 millivolts and opposes the general E. M. F. of the cell, as expected from a moderate concentration of OH ions. In ratios 1:3 and 1:4

¹ J. Phys. Chem., 30, 1100 (1926).

the P. D. is just as large but is in the opposite direction. Here the OH ion concentration is practically negligible, hence the silicate ion is less mobile than the sodium, or there is a greater concentration of sodium ions present.

We have seen, too, that when the percentage hydrolysis is plotted against the ratio somewhat similar changes of direction occur as when the conductivity is plotted against the ratio, and the conclusion was drawn that the variation in conductivity noted, in the more concentrated solutions of ratios containing little silica, are mainly due to changes in the OH ion concentration.

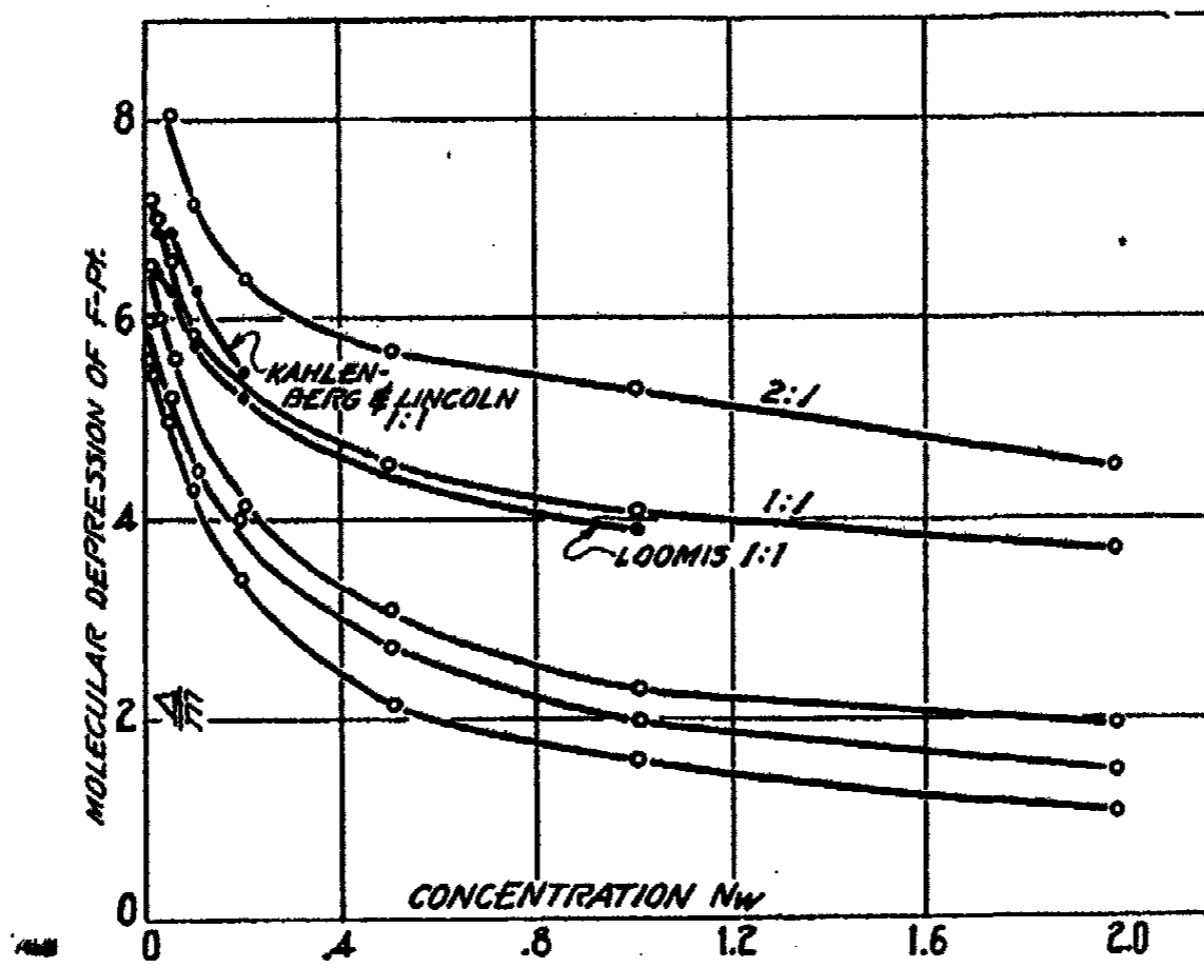


FIG. 4
Molecular Depression of Freezing Point against Concentration

(5) *Osmotic Activity.*

Lowering of vapour pressure and freezing points.

In Part V of this series¹ are described measurements of the lowering of the vapour pressure and of the freezing point, the results summarised below being presented from the point of view of both the earlier ionic theory, Table VI, and from the more recent activity theory, Table VII.

These results are shown graphically in Fig. 4.

These results show us that for ratio 1:1 both modes of calculation indicate that at concentration 0.01 N_w dissociation into 4 ions or active constituents is nearly complete and accounts for the conclusions of early investigators that Na_2SiO_3 was almost completely hydrolysed according to the following equation,—

¹ J. Phys. Chem., 31, 355 (1927).

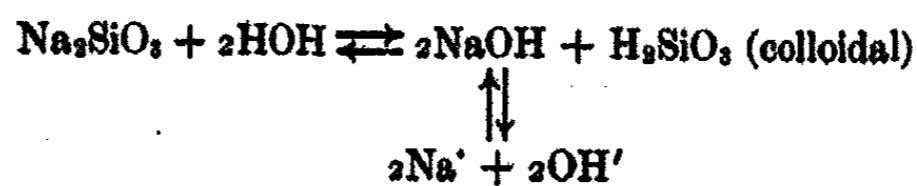


TABLE VI
Lowering of the Freezing Point

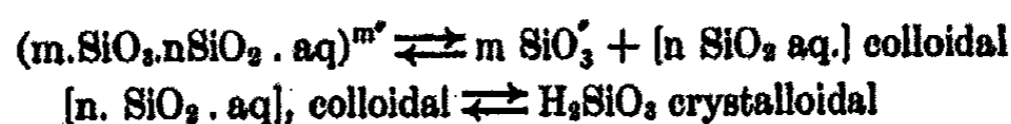
| N _w | m | Van't Hoff factor "i". | | | | |
|----------------|-------|------------------------|------|------|-------|-------|
| | | 2:1 | 1:1 | 1:2 | 1:3 | 1:4 |
| 2.00 | 1.00 | 2.30 | 1.98 | 1.03 | 0.772 | 0.565 |
| 1.00 | 0.50 | 2.85 | 2.19 | 1.22 | 1.06 | 0.855 |
| 0.50 | 0.25 | 3.05 | 2.45 | 1.67 | 1.46 | 1.06 |
| 0.20 | 0.10 | 3.45 | 2.88 | 2.19 | 2.17 | 1.83 |
| 0.10 | 0.05 | 3.85 | 3.13 | 2.74 | 2.36 | 2.13 |
| 0.05 | 0.025 | 4.35 | 3.55 | 3.01 | 2.73 | 2.69 |
| 0.02 | 0.01 | 5.05 | 3.75 | 3.22 | 2.96 | 2.96 |
| 0.01 | 0.005 | 5.60 | 3.87 | 3.55 | 3.22 | 3.01 |

TABLE VII
Activity Coefficient, from F. Pt. based on $\nu = 4$, i.e. the molecule gives 4 ions at infinite dilution

| m | NaOH | 1:1 | 1:2 | 1:3 | 1:4 |
|-------|-------|-------|-------|-------|-------|
| 0.005 | 0.950 | 0.922 | 0.731 | 0.604 | 0.412 |
| 0.010 | 0.920 | 0.888 | 0.599 | 0.484 | 0.342 |
| 0.025 | 0.867 | 0.778 | 0.456 | 0.359 | 0.244 |
| 0.050 | 0.820 | 0.626 | 0.358 | 0.252 | 0.171 |
| 0.100 | 0.765 | 0.497 | 0.259 | 0.179 | 0.109 |
| 0.500 | 0.700 | 0.280 | 0.080 | 0.052 | 0.029 |
| 1.000 | 0.680 | 0.192 | 0.035 | 0.029 | 0.015 |

But this view is no longer tenable, as not being in accord with the percentage hydrolysis as directly measured. In the paper on hydrolysis (*loc. cit.*) it was shown that ratio 1:1, i.e. the metasilicate, Na_2SiO_3 , undergoes on solution both ionic and hydrolytic dissociation giving rise to Na , OH and SiO_3 ions and crystalloidal H_2SiO_3 , at least in dilute solution.

It was there shown, too, that, as far as hydrolysis, sodium ion activity, and freezing point lowering results are concerned, it appeared very probable that the acid salt NaHSiO_3 exists in solution. Ratios 1:3 and 1:4 on the other hand do not appear to be definite salts and their behaviour in solution is quite remarkable, e. g. the van't Hoff factor "i" for ratio 1:4 ranges from 0.565 for 2 N_w to 3.01 for 0.01 N_w, while the activity coefficient ranges from 0.015 to 0.412 for the same concentrations respectively. To explain this it was there tentatively put forward that the results from ratios 1:3 and 1:4 seemed to suggest the possibility of complex colloidal aggregates in very concentrated solution, and of ionic micelles in moderately concentrated solutions, such ionic micelles breaking up on dilution somewhat after the manner indicated by the following equations,—

(6) *Heterogeneous Equilibria.*

System: $\text{Na}_2\text{O} : \text{SiO}_2 : \text{H}_2\text{O}$ at 25°C .

In this paper¹ (Part VI) it was shown that only two salts corresponding to ratios 1:1 and 1:2 exist at 25°C . Ratio 1:1 is undoubtedly the metasilicate, Na_2SiO_3 , and its hydrates have been shown to contain 9, 6 and 2.5 aq respectively. Ratio 1:2 may be either $\text{Na}_2\text{Si}_2\text{O}_5$ or NaHSiO_3 , but in any case should crystallise out with the composition $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 9\text{H}_2\text{O}$.

No evidence for the existence of any other than salts corresponding to these two ratios was found.

Attention was drawn in this paper to the fact that Morey had previously obtained Na_2SiO_3 and $\text{Na}_2\text{Si}_2\text{O}_5$, and these two only, but his $\text{Na}_2\text{Si}_2\text{O}_5$ was not readily affected by water. It was also noted that both Niggli and Wallace failed to obtain a definite salt richer in silicate than the metasilicate.

(7) *Silicate Ions and Crystalloidal Silica.*

The problem of obtaining some definite knowledge on this aspect of the problem is treated in Part VII of this series² but only in a meagre preliminary manner.

The electrometric titration curves of a dilute HCl solution against dilute Na_2SiO_3 solutions are typical of dibasic acids, thus suggesting H_2SiO_3 as a true dibasic acid with salts NaHSiO_3 and Na_2SiO_3 ; the dissociation constants being given as $k_1 = 4.2 \times 10^{-10}$ and $k_2 = 0.51 \times 10^{-10}$.

The results from a few diffusion experiments indicate that most of the silica in ratios 1:1 and 1:2 is diffusible, about $\frac{2}{3}$ of the silica in 0.3N 1:4 and about $\frac{1}{3}$ in 0.1N H_2SiO_3 being crystalloidal.

In this paper, also, a colorimetric method of estimating crystalloidal silica by means of H_2SO_4 and ammonium molybdate showed that the amount of crystalloidal silica in any ratio was directly proportional to and expressed by the same figure as the ratio $\text{SiO}_2:\text{Na}_2\text{O}$ in extremely dilute solution.

Theoretical

An attempt will now be made to correlate the data obtained and to present an explanation of the constitution and of the behaviour in aqueous solution of the various $\text{Na}_2\text{O}:\text{SiO}_2$ ratios investigated. Attention will be chiefly focussed on the evidence adduced in proof of the following four main statements,—

(1) Silica exists in solutions of these ratios not wholly colloidal as heretofore supposed, but wholly or partly as crystalloidal silica depending upon the ratio $\text{Na}_2\text{O} : \text{SiO}_2$ and upon the concentration. This crystalloidal silica existing in equilibrium with silicate ions, or electrically charged aggregates of silicate ions and silica i.e. ionic micelles, or pure colloidal aggregates, as the case may be, depending upon the ratio and concentration.

¹ J. Phys. Chem., 31, 511 (1927).

² J. Phys. Chem., 31, 616 (1927).

(2) In aqueous solution at 25° C two and only two simple salts viz., Na_2SiO_3 , i.e. ratio 1:1, and NaHSiO_3 , i.e. ratio 1:2, appear to exist as such, the behaviour and nature of which are now elucidated.

(3) Ratios other than 1:1 and 1:2 are not definite salts but are typical examples of colloidal electrolytes.

(4) The fundamental nature of silica in solution appears to depend upon the existence, at least in the range here investigated, of only one acid, metasilicic acid, in which the equilibrium between the crystalloidal and the colloidal constituents depends upon the concentration, the crystalloidal content at ordinary concentrations being much greater and the acid, therefore, much stronger, than generally supposed.

Evidence for the Existence of "Crystalloidal" Silica¹

Under the heading "crystalloidal silica" are classed definite silicate ions, aggregates of ions carrying an electric charge with or without some colloidal silica, i.e. ionic micelles, and crystalloidal silicic acid or hydrated silica. The evidence produced herein, for the existence of such crystalloidal silica, rests mainly on the following four sources,—

(1) Conductivity measurements resulted in the finding of a much greater conductivity for ratios up to 1:2 than could result alone from the proportion of NaOH formed by hydrolysis, as measured by the E. M. F. method. Above ratio 1:2 where the hydroxyl ion concentration is very low, the sodium ion accounts for about only one-half the conductivity found. The only way to account for the conductivity is to postulate the existence of silicate ions with mobilities ranging from 40-60 approximately. Moreover, the equivalent conductivity, as calculated from the concentration of sodium, hydroxyl and silicate ions as found from F. Pts., OH and Na ion measurements, and their respective mobilities, agrees well with the experimentally determined conductivity.

(2) The most direct and conclusive evidence so far put forward to show that the silica in aqueous solutions of these ratios carries an electric charge is obtained from the results of transport number experiments. From these it was shown that $n_{\text{sil}} = 0.16$ for ratio 1:1, 0.41 for ratio 1:2, 0.46 for 1:3, and 0.59 for 1:4, when calculated by the second method. Whether this basis of calculation is correct or not, these transport number experiments proved that quite a fair proportion of the current, at least one-half in the higher ratios, is carried by the "silica." Since the possibility of adsorbed hydroxyl ions on the silica giving the necessary charge to the silica, has been shown to be remote and indeed most improbable, the only conclusion is that the silica must exist as ions. The relatively high mobility of these charged silica particles as deduced from conductivity and transport number results, is also contrary to that expected from colloidal aggregates with OH ions adsorbed thereon.

(3) A third very weighty argument appears when we consider the result of hydrolysis experiments along with freezing point lowering results. In

¹ In this paper the word "crystalloidal" is used to denote constituents which are "osmotically and ionically active."

the paper on osmotic activity it was shown that the only possible way to account for the high osmotic activity of these ratios in aqueous solution was to accept the existence of silicate ions. The conductivity of the sodium ions and of the hydroxyl ions as found by E. M. F. experiments, together account for only a fraction of the total ion concentration as determined by freezing point lowering. The non-accordance is quite beyond the bounds of experimental error, nor could it be accounted for by the assumptions underlying the laws governing ideal solutions. The higher the ratio the wider is the divergence, so that in 1:3 and 1:4 more than half the "crystalloidal" content has to be accounted for by the silica in the more dilute solutions. Whether this is due to the complex silica aggregates breaking down into simpler silicate ions, or to the disintegration of an ionic micelle, or to crystalloidal H_2SiO_3 ionising, or to all these phenomena, will be discussed later. The fact remains, however, of a very large proportion of crystalloidal silica in solution, more especially in dilute solution.

(4) Direct evidence of the existence of crystalloidal silica is put forward in Part VII of this series, giving the results of diffusion experiments with colloidion membranes and parchment paper, and the results of a colorimetric estimation for crystalloidal silica based on the formation of silicomolybdate. The diffusion experiments indicated that most of the silica in ratios 1:1 and 1:2 is diffusible; about $\frac{2}{3}$ of the silica in 0.3 N_w 1:4 and about $\frac{1}{3}$ in 1.0 N_w H_2SiO_3 also being crystalloidal. The silicomolybdate colorimetric test showed that in very dilute solution, 0.001N_w, the amount of crystalloidal silica as compared with that in ratio 1:1 i.e. sodium metasilicate, was directly proportional to the ratio.

The existence of crystalloidal silica and silicate ions in aqueous solution seems therefore firmly established, and there now remains the problem of what nature and composition are the ions and charged aggregates, and in what proportions they exist. In the solution of this problem the nature and composition of the salts giving rise to these ions furnish a good guide, and help to narrow down the possibilities.

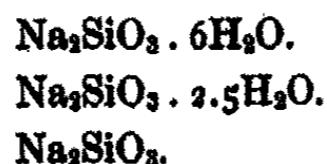
Ratios 1:1 and 1:2 are Definite Salts. Their behaviour in solution.

From the investigation of the ternary system $Na_2O : SiO_2 : H_2O$ at 25°C we have seen that only ratios 1:1 and 1:2 occur as definite solid salts. Ratio 1:1 is the metasilicate Na_2SiO_3 , crystallising with 9, 6 and 2.5 aq., the existence of which has long been established, in spite of the difficulty of its crystallisation and the confusion which till now has existed concerning its hydrates.

A certain amount of evidence that these two ratios correspond to definite salts in solution is also forthcoming from consideration of the curves where conductivity, hydroxyl ion concentration, sodium ion concentration, and the van't Hoff factor "i" (from freezing points) are severally plotted against the ratio, distinct changes of direction at these points being evident. It was also seen from consideration of freezing point results that the existence of salts corresponding to ratios 1:3 and 1:4 was very unlikely.

From these results of the phase rule investigation we have seen that the following solid salts would be expected to separate from solution,—

(1) $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$. This salt has been obtained by the author not only from alcoholic solution, but also in the form of large, well-defined crystals from a 2 N_w solution of ratio 2:1 without the addition of alcohol or inoculating crystals.



This decides the hitherto conflicting and confusing data concerning the hydrates of Na_2SiO_3 .

(2) $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 9\text{H}_2\text{O}$. This compound has so far resisted all attempts at separation in a pure form from aqueous solution at 25°C. It may be from the phase rule results, either $\text{NaHSiO}_3 \cdot 4\text{H}_2\text{O}$ or $\text{Na}_2\text{Si}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$.

Ratios 1:3 and 1:4.

We have seen that only the ratios 1:1 and 1:2 exist as definite silicates and there now remains an explanation of ratios 1:3 and 1:4.

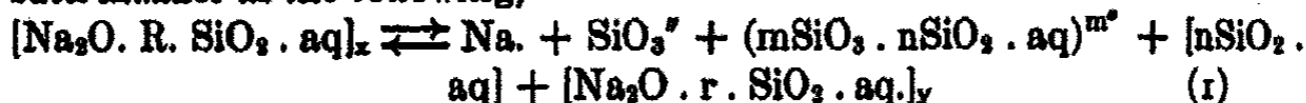
The fact that there is increasingly less percentage hydrolysis as the proportion of silica increases in the ratio until it is practically negligible in 1:4 favours very much the view that these higher ratios are complexes of the two beforementioned salts with excess of silicic acid, or hydrated silica, the presence of the silicic acid, one of the products of hydrolysis of these two salts, causing the diminution in hydrolysis according to the law of mass action.

Again, if either of the ratios 1:3 or 1:4 were definite salts, then, since, hydrolytic decomposition seems negligible, 100% ionisation into three ions would not be sufficient to account for the large molecular depression of the freezing point in dilute solution. However, sodium ion activity measurements indicate that in dilute solution 70% in ratio 1:3 and only 55% in 1:4 is the extent to which the sodium exists as active sodium ions. To bring the results from F. Pt. measurements and from sodium ion measurements into agreement would necessitate, since only sodium and silicate ions are present, in the case of ratio 1:3 approximately 80% ionisation into 4 ions, and in 1:4 approximately 60% ionisation into 5 ions. It appears quite improbable that any simple salt of composition corresponding to ratio 1:3 i.e. $(\text{Na}_2\text{O} \cdot 3\text{SiO}_2 \cdot \text{aq.})_n$ could ionise into 4 ions or any corresponding to 1:4 i.e. $(\text{Na}_2\text{O} \cdot 4\text{SiO}_2 \cdot \text{aq.})_n$ into 5 ions. Nor would it be a reasonable hypothesis even to assume the existence of such problematical compounds when all the evidence (except for the results of experiments on transport numbers) from the other lines of investigation employed, goes against the existence of these higher ratios as definite salts.

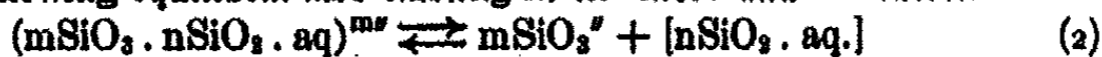
Thus an explanation on quite different lines must be sought, and a most rational one follows when we consider these ratios as colloidal electrolytes from the viewpoint of aggregate or micelle formation.

Silicates as Colloidal Electrolytes

In very concentrated solution the silicate probably exists as a very complex aggregate, which not only breaks up into similar simple aggregates on dilution but also gives rise to sodium and SiO_2 ions and ionic micelles, in some such manner as the following, =



The following equilibria also existing in the more dilute solution



where aggregates included in square brackets are colloidal.

Dilute Solution 1:4.

Since $\gamma = 0.55$ at concentration $N_w = 0.01$ from sodium ion activity measurements, and since there must be two sodium ions for each SiO_2 ion or $(m\text{SiO}_2 \cdot n\text{SiO}_2 \cdot \text{aq})^{m'}$ aggregate, the total normality of ion constituents is thus $3 \cdot N_w \cdot \gamma = 0.0165 N_w$. But the total crystalloidal content is $0.03 N$ from F. Pt. measurements, so there is still $0.0135 N$ crystalloidal content to account for. Part of this is no doubt due to the unionised $(\text{Na}_2\text{O} \cdot 3\text{SiO}_2 \cdot \text{aq})$ which at this dilution may be supposed broken down into a more or less simple or crystalloidal condition. If it were all so i.e. $0.0045 N$ in this simple state there is still $0.009 N$ crystalloidal matter to account for. The only rational assumption to account for this $0.009 N$ crystalloidal matter is to consider it a simple or unionised hydrated silica or silicic acid, probably H_2SiO_3 , as postulated in equation (3) above. This means that $\frac{0.009}{0.04} = 0.225$ or 22.5% of the total

silica is in the form of H_2SiO_3 . If none of the unionised $(\text{Na}_2\text{O} \cdot 3\text{SiO}_2 \cdot \text{aq})$ is in a simple crystalloidal condition then there is $0.0135 N$ silicic acid i.e. 34% or 34% of the total silica present.

Thus at concentration $0.01 N_w$ 1:4 ratio, we have approximately 34% of the total silica in the crystalloidal form of H_2SiO_3 , and 14% in the crystalloidal form of ions or ionic micelles, i.e. about 50% as crystalloidal silica. This amount of crystalloidal and colloidal silica, 50%, receives direct support from the colorimetric estimation of crystalloidal silica in the form of silicomolybdate, (paper VII) where it was shown that about 75% of the silica is crystalloidal at concentration $0.007 N_w$ ratio 1:4.

Dilute Solution 1:3.

Similarly for a $0.01 N_w$ solution 1:3, we get a total crystalloidal content of $0.032 N$ from F. pts., and a crystalloidal content of 0.014 for sodium ions from activity measurements, leaving $0.018 N$ to be accounted for by the silica content of $0.03 N_w$. Thus $\frac{0.012}{0.030}$ or 40% of the total silica is colloidal.

The colorimetric estimation shows that nearly 20% of the total silica is colloidal at concentration $0.007 N$, so here also the colorimetric method gives a lower value, due no doubt to the error incurred in attempting to measure these relatively high concentrations by its means.

Moderately Concentrated Solutions.

It was for concentrations 1.0-0.1 N_w that the transport numbers were found and from which we concluded that in ratios 1:3 and 1:4 there were three and four equivalents SiO_2 respectively, per electric charge. It is in these solutions that the micelle or aggregate would evidence itself if it existed.

From sodium ion measurements 25% of the total sodium is in an active ionic form and hence 25% of the total silica is also in an active ionic form, presumably $(m\text{SiO}_2 \cdot n\text{SiO}_2 \text{ aq})^{m-}$ from transport experiments: these two giving rise to 0.075 N crystalloidal matter, leaving 0.155 N = crystalloidal matter to be accounted for by the remaining 0.3 N_w silica and 0.075 N_w sodium content, which means that about 50% of this remaining silica or 30% of the total silica is in the colloidal form associated probably with sodium.

From diffusion experiments we have seen that about $\frac{1}{3}$ of the total silica is in the colloidal form at concentration 0.3 N_w 1:4. Although the results obtained and the calculations and conclusions therefrom given above, do not afford absolute and conclusive proof of the two fundamental suggestions upon which this theory of the behaviour of sodium silicates in solution rests, viz., (1) the existence of a micelle or aggregate of the composition $(m\text{SiO}_2 \cdot n\text{SiO}_2 \cdot \text{aq})^{m-}$ (2) simple unionised crystalloidal hydrated silica, H_2SiO_3 , or other silicic acids, yet considering all the experimental evidence to date one is forced to acknowledge that only along some such lines can the behaviour of these solutions be explained.

The reasons for assigning such a constitution as the above to these silicate solutions are briefly recapitulated again,—(1) no evidence has been found experimentally to show that definite salts corresponding to ratios 1:3 and 1:4 in particular, and to the ratios higher than 1:2 in general, exist in solution at 25°C (2) the transport numbers indicate that the number of mols of SiO_2 per divalent charge is approximately numerically equal to the ratio $\text{Na}_2\text{O} : \text{SiO}_2$.

(3) The conductivity in dilute solutions is very good and as there is no OH ion and the sodium ion accounts for a little less than half of the conductivity, silicate ions or charged aggregates of fairly large mobility must exist.

(4) In concentrated solution the conductivity, sodium ion concentration, crystalloidal content (from freezing-points measurements) are all most abnormally low, yet all surprisingly high in dilute solution, such that ionisation into sodium ions and equivalent silicate ions, as measured by the sodium ion concentration, shows a serious discrepancy with freezing point lowering results, unless we consider that complex silicate ions or micelles exist in the stronger solution and split up into simpler crystalloidal states in dilute solution.

(5) A fair agreement exists between the relative amounts of colloidal and crystalloidal silica calculated from the osmotic activity measurements on the two assumptions of the existence of a micelle and crystalloidal silica, and those found directly by colorimetric estimation and by diffusion.

(6) Simple unionised crystalloidal silicic acid has been shown to exist at much higher concentration than usually granted; it is also a much stronger acid than hitherto supposed.

(7) The widely recognised property of silicon or silica and its hydrates to form complexes, molecular compounds and aggregates, colloidal solutions and gels, would seem to be in agreement with the conclusions here set forth.

Concentrated Solutions.

The concentrated solutions of these ratios are characterised by a very low conductivity, practicable negligible hydrolysis, very low sodium ion concentration, abnormally low molecular depression of the freezing-point, very high viscosity, and non-diffusibility, facility to form the gel condition etc., in fact getting more and more typically colloid either with increase of concentration or with increase of SiO_2 in the ratio.

The theory here outlined affords a good explanation of this, in fact it is necessary only to recall that at the lower concentrations we have seen that the equilibria represented by equations (1), (2) and (3) at the head of this section all show a tendency to go from right to left with increasing concentration in any one ratio, and with increasing ratio $\text{SiO}_2 : \text{Na}_2\text{O}$ at any one concentration.

Such being the case it is a natural consequence to expect solutions of any ratio to become more and more colloidal as the concentration increases and to expect the colloidal properties to be evidenced earlier and in more marked respect the higher the ratio.

The transition from a typical colloid, through the colloidal electrolyte stage to a good electrolyte is very well shown by ratio 1:4 on diminishing the concentration. Ratio 1:3 also shows the transition well and it seems permissible to carry the analogy to the lower ratios, where it is seen to offer the best explanation of the very viscous solutions of ratio 1:1 and its low conductivity and osmotic activity.

Summary

(1) A summary is given of the results and conclusions of seven preceding papers on the aqueous solutions of sodium silicates of ratios 2:1 to 1:4 at concentrations ranging from 0.001 N_w to 2.0 N_w , from the points of view of conductivity, transport numbers, sodium ion activity, hydrolysis, osmotic activity, phase rule, and crystalloidal silica.

(2) The various data have been correlated and an explanation given of the constitution and behaviour in aqueous solution of these silicates.

(3) The evidence for crystalloidal silica and silicate ions has been recapitulated.

(4) Ratios 1:1 and 1:2 only are definite salts viz., Na_2SiO_3 and NaHSiO_3 and their percentage hydrolysis and ionisation have been found and shown to agree with the various measurements, thus affording a complete explanation of their behaviour in solution.

(5) Above ratios 1:2 colloidal silica is in evidence, the proportion of colloidal silica increasing with the concentration and the ratio $\text{SiO}_2 : \text{Na}_2\text{O}$.

(6) In dilute solutions of ratios above 1:2 crystalloidal uncharged silica probably H_2SiO_3 or simple hydrated silica occurs.

(7) These ratios higher than 1:2 exhibit properties characteristic of colloidal electrolytes with a micelle of the composition $(mSiO_2 \cdot nSiO_2 \cdot aq.)^m$

where $\frac{m+n}{m} = \text{ratio } SiO_2/Na_2O$.

(8) In concentrated solutions of the higher ratios a large colloidal aggregate exists, containing both sodium and silica.

(9) Silicic acid has been shown to be stronger than usually supposed, its dissociation constants being of the order 10^{-10} and 10^{-16} .

I wish to express my thanks to the Commissioners of the 1851 Exhibition for a scholarship which has enabled me to carry out this work, and to Professor Donnan for his constant, kindly interest and advice.

*The Ramsay Laboratories of Physical and Inorganic Chemistry,
University College, London.
May 30, 1927.*

THE HEATS OF VAPORIZATION OF ISO-PROPYL ALCOHOL AND ETHYL ALCOHOL

BY GEORGE S. PARKS AND WILLIAM K. NELSON

A few years ago, in connection with another research, some information was needed concerning the heat of vaporization of iso-propyl alcohol. At that time the only two values existing in the literature were those of Luginin¹ and Brown.² The former reported a result of 157.8 cal. per gram; the latter obtained a mean value of 161.1 in a very careful and noteworthy investigation of the heat of vaporization of a number of substances. It seemed to us probable that these earlier investigators may have been seriously handicapped in obtaining accurate values by the difficulty attached to securing any large amount of pure iso-propyl alcohol. At any rate there is a 2% discrepancy between their results; and, in view of this situation, the present determination was undertaken. As will be shown subsequently in this paper, our mean result is 161.7 cal. per gram.

In making the determinations to be described, ethyl alcohol was used for preliminary measurements in order to test the apparatus and to aid in remedying any sources of error that might become apparent. This was done because the supply of ethyl alcohol was more plentiful than that of iso-propyl alcohol. However, it was found that the values previously obtained for the heat of vaporization of ethyl alcohol showed great divergence, so after the development of our method two complete series of runs were made upon this substance. Our mean result in this case was 208.7 cal. per gram.

Following the completion of our work, Mathews³ has recently published the data of a very interesting investigation on the heat of vaporization of a large number of liquids. For iso-propyl alcohol he obtained 159.23 and for ethyl alcohol 201.88 cal. per gram at the respective temperatures, 81.25° and 77.42° C.

Experimental

Materials. Commercially refined iso-propyl alcohol and ethyl alcohol served as the starting point in the preparation of the materials for the present investigation. Water being the chief impurity, these were first dehydrated by three successive treatments and distillations with lime in the ordinary manner. The resulting liquids were then carefully fractionated. In each instance the middle fraction, about 60% of the total, was selected for use in the measurements. It showed a density of 0.78108 $25^{\circ}/4^{\circ}$ in the case of iso-propyl alcohol and of 0.78549 $25^{\circ}/4^{\circ}$ for ethyl alcohol. On the basis of the criteria⁴ previously employed, these values correspond to a purity of 99.90% and 99.86%, respectively.

¹ Luginin: *Ann. Chim. Phys.*, (7) 13, 340 (1898).

² Brown: *J. Chem. Soc.*, 83, 991 (1903).

³ Mathews: *J. Am. Chem. Soc.*, 48, 572 (1926).

⁴ Parks and Kelley: *J. Phys. Chem.*, 29, 728 (1925).

Apparatus and Procedure. In principle, the method was simple. It consisted essentially of supplying measured quantities of heat electrically to the alcohol, which previously had been brought to its boiling point, and of condensing and weighing the amount thereby vaporized. Thus, a careful weighing of the amounts vaporized per 15-minute period at two known rates of energy input gave, by difference, the necessary data for the calculation of the heat of vaporization.

The apparatus, as finally developed after much preliminary experimentation, conformed closely to the second type described by Awbery and Griffiths.¹ A 2.5-liter, silvered, Dewar vessel served as the container for the alcohol which was to be vaporized. This vessel was of a carafe or bottle shape with a neck about 12 cm. long. Thus, with the carafe half-filled with liquid, the vapor produced had to pass vertically upward at least 20 cm. before escaping into the outlet tube. This distance should greatly reduce any error due to the production of spray and the consequent loss of liquid as such. The heating coil in this evaporator consisted of 1.5 meters of No. 30 (B. and S.) enameled Therlo wire, wound upon a small mica frame; it had a resistance of about 14 ohms. The carafe was fitted with a cork stopper (tin-foiled) which carried the mercury-filled glass tubes leading to the heating coil, a glass tube closed at the lower end and containing a thermocouple junction for measuring the temperature of the liquid, and a 12 mm. Pyrex outlet tube for the vapor. The last ran through the stopper vertically, then turned sharply downward at an acute angle and passed out through an opening in the outer jacket to connect with an inclined condenser.

Surrounding this Dewar evaporator was the outer container or thermostat, which was a vapor-tight, cylindrical vessel of copper about 60 cm. high and 20 cm. in diameter. It was jacketed with a layer of asbestos sheeting. The upper half of this container was then wound with a few turns of high resistance wire to serve as a heating coil and covered with another layer of sheeting. A form, wound with more resistance wire, covered the top of the cylinder. These coils, placed in parallel with one another but in series with a variable resistance, were supplied with a suitable current from the 110-volt line. The outer container was ordinarily filled to a depth of about 3 cm. with some of the same alcohol employed in the evaporator. During the vaporization measurements this liquid was heated and kept at its boiling point by means of a Bunsen burner placed directly beneath the cylinder, which rested upon a small iron tripod. To conserve the resulting vapor, the outer container was equipped with a reflux condenser, the connecting tube being large enough to insure smooth boiling and the easy return of condensed alcohol. The Dewar evaporator, being a commercial vacuum bottle, came supplied with a small metal jacket and this was left on in the present case to prevent any of the cooled condensate from coming into direct contact with the glass vessel.

In addition to the openings for the outlets to the two condensers, there were two more openings in the copper cylinder for the lead wires to the heat-

¹ Awbery and Griffiths: Proc. Phys. Soc. London, 36, 309 (1924).

ing coil within the evaporator. Two wires were led in through each of these two openings. One pair of wires carried the current from the lead storage battery and the other pair connected with the voltmeter which was used to measure the fall of potential across the heating coil. All openings in the outer container were reinforced by soldering in short pieces of copper tubing of such diameters that standard rubber stoppers gave very tight seals. The lead wires were introduced through these stoppers as were also the glass outlet tubes for the liquid. The container was fitted with a leak-proof cover.

A flat wooden block was used as a stand for the Dewar evaporator inside the copper cylinder. This block was drilled in several places to permit free circulation of the bath liquid. As noted before, the outer container was mounted upon an iron tripod stand. The condensers were supported by large iron ringstands.

A large piece of asbestos was formed into a cylindrical screen about 90 cm. high and 40 cm. in diameter. Holes were made in this screen for the lead wires and the outlets to the condensers, and it was then placed around the entire apparatus. A circular piece of asbestos sheeting was used to cover the top.

The copper-constantan thermocouple wires were led into the outer container through the reflux condenser and from there to the tube in the stopper of the Dewar carafe. The other junction was placed in a mixture of ice and water. The e. m. f. readings were made with a Leeds and Northrup "thermocouple" potentiometer. The voltmeter employed for determining the fall of potential across the heating coil in the evaporator was a Weston instrument, reading to 0.01 volt. The ammeter, in series with the coil, was of German manufacture and could be read to 0.001 ampere. The time elapsing during the collection of a sample of the condensed vapor was measured by a stopwatch. The voltmeter, ammeter and watch were carefully calibrated at the time of the determinations and probably gave values for the energy input accurate to within 0.3%.

The actual procedure in making the measurements of the heats of vaporization was extremely simple. The evaporator was about half filled with the particular alcohol under investigation. Enough of the same material was kept in the outer container to prevent it from becoming dry through evaporation losses, although the level was always maintained below the bottom of the Dewar carafe. The quantities of liquid in the two vessels having been satisfactorily arranged, the apparatus was heated up to the boiling point of the alcohol. To accomplish this the outer container was heated by means of the Bunsen burner and the external heating coils, while heat was supplied to the alcohol in the carafe by an electric current from a 20-volt storage battery discharging through the Therlo coil. After the condensate from the evaporator began to flow at a uniform rate and the thermocouple gave a reading corresponding to the boiling point of the alcohol, the applied voltage was reduced to approximately two volts. A half-hour was allowed to elapse, in order that equilibrium might be attained, and then the condensate was collected in small Erlenmeyer flasks and weighed. In each set of determina-

tions five portions were collected at this voltage, fifteen minutes being the duration of each collection period. The voltage was next increased to the figure at which the measurement was to be made, and another half-hour was devoted to securing equilibrium. At the end of this interval the condensate was again collected over fifteen minute periods and weighed. Eight or nine portions were usually taken during a series of the determinations, great care being exercised to change the flasks at exactly the end of the fifteen minute periods without loss of liquid. The voltmeter and ammeter were read at one minute intervals during the collection of each sample of condensate and the average of these readings was taken for the calculations. The energy input at two volts and the amount of liquid collected at this voltage were used as reference quantities; the values thereby obtained were subtracted from those found for the higher voltages. Under these experimental conditions there could be but little energy exchange between the evaporator and its surroundings and the residual effect was allowed for by thus determining the energy required to produce a very slow rate of evaporation.

Results. The individual results obtained in one of the series of determinations on iso-propyl alcohol are recorded in Table I. In order to show the calculation involved, it may be well to indicate the steps taken to find the first of these:

| | |
|-------------------------------------|---------------|
| Average lower voltage | 1.940 volts |
| Average lower current | 0.141 amps. |
| Average condensate at lower voltage | 0.700 gms. |
| Average higher voltage | 13.585 volts |
| Average higher current | 0.987 amps. |
| Condensate at higher voltage | 18.158 gms. |
| Time of collecting sample | 900.0 seconds |

$$\text{Heat of vaporization} = \frac{[(13.585)(0.987) - (1.940)(0.141)](0.2391)(900)}{(18.158 - 0.700)}$$

$$= 161.9 \text{ cal./gm. (preliminary value).}$$

To correct for the current passing through the voltmeter circuit and for the heat lost in the leads to the Therlo coil, we must now reduce this value by 1.5%. Thus, the final result becomes 159.5 calories per gram.

TABLE I

Heat of Vaporization of Iso-Propyl Alcohol

The individual results obtained in Series C.

| Determination number | Heat of Vaporization | Determination number | Heat of Vaporization |
|-------------------------|----------------------|----------------------|----------------------|
| 1 | 159.5 cal. | 5 | 161.5 cal. |
| 2 | 161.9 " | 6 | 161.2 " |
| 3 | 161.2 " | 7 | 161.7 " |
| 4 | 160.8 " | 8 | 161.9 " |
| Mean result of Series C | | | 161.21 " |

In Table II we have summarized our experimental results for five series of determinations on iso-propyl alcohol and two series on ethyl alcohol. The data given serve to indicate the type of concordance obtained in successive series of determinations.

TABLE II
Summarized Data for the Heats of Vaporization of Iso-Propyl Alcohol and of Ethyl Alcohol

| Determinations | Mean voltage | | Mean wt. of condensate | | Mean heat of vaporization |
|---------------------------|--------------|-------|------------------------|-------|---------------------------|
| | Higher | Lower | Higher | Lower | |
| <i>Iso-Propyl Alcohol</i> | | | | | |
| Series A | 12.914 | 1.892 | 16.282 | 0.675 | 161.04 cal. |
| B | 12.846 | 1.882 | 16.194 | 0.869 | 162.30 " |
| C | 13.586 | 1.940 | 17.990 | 0.700 | 161.21 " |
| D | 11.596 | 1.942 | 13.299 | 0.872 | 162.00 " |
| E | 11.488 | 1.924 | 12.993 | 0.809 | 162.10 " |
| Final mean value | | | | | 161.73 " |
| <i>Ethyl Alcohol</i> | | | | | |
| Series A | 13.147 | 1.912 | 13.190 | 1.015 | 208.82 cal. |
| B | 13.117 | 1.912 | 12.903 | 0.789 | 208.52 " |
| Final mean value | | | | | 208.67 " |

Discussion

As shown in the preceding table, our mean result for the heat of vaporization of iso-propyl alcohol is 161.7 calories per gram at its boiling point (82.2°). Luginin and Brown in earlier investigations obtained 157.8 and 161.1 calories, respectively. Of these two values, that of Brown is undoubtedly the more trustworthy because of the relatively great care and precision of his experimental method. The recent result of Mathews, 159.23 cal. at 81.25°, appears to be the product of an extremely refined apparatus and a painstaking procedure, although from his paper it is not clear that he was able to entirely avoid the production of fog or spray in the vaporization process. Of course, such spray tends to produce results that are too low and has constituted one of the major sources of error in past calorimetric determinations of heats of vaporization. However, in the present case this may not be the cause of the discrepancy between our result and that of Mathews, for it appears that he used material that differed appreciably from ours. He reports a density of 0.7830 25°/4° for his iso-propyl alcohol and this, on the basis of our own standards of purity (essentially the density determination of Brunel¹), corresponds to a liquid containing 0.94% water. Taking all these points into consideration, we therefore would like to suggest 161.0 (±1.5) calories per gram as the most likely value for the heat of vaporization of iso-propyl alcohol.

In the case of ethyl alcohol, our mean result is 208.7 calories at the boiling point, 78.4°. The more important earlier values² are 201.5 (Luginin), 205.1

¹Brunel: J. Am. Chem. Soc., 45, 1336 (1923).

²Landolt-Börnstein-Roth-Scheele: "Tabellen," 1480 (1923).

(Wirtz), 206.4 (Schall), 207.2 (Young), 216.5 (Marshall and Ramsay) and 216.4 (Brown). Mathews' recent determination gave 201.88 at 77.4°. The average of all these results, 207.9 calories, agrees very well with our own value and is about midway between those so carefully obtained by Brown and by Mathews. Hence, as a provisional value for use at the present time, 208 calories per gram is probably as satisfactory and reasonable as any other that might be suggested. However, in the case of a very common and important substance like ethyl alcohol, such a marked variation in the experimental results is extremely unfortunate; certainly the situation requires further research for its clarification.

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July 1, 1927.*

EQUILIBRIUM IN ELECTROLYTE SOLUTIONS

BY FREDERICK GEORGE SOPER

The condition which must be satisfied by all systems in true equilibrium is that the Free Energy change occasioned by a slight displacement of the system from the equilibrium position, is zero. Application of this principle to homogeneous equilibria of the type, $A + B + \dots \rightleftharpoons P + Q + \dots$, leads to the equation

$$F_A + F_B + \dots = F_P + F_Q + \dots \quad (1)$$

where the F 's denote the partial free energies, as a definition of the equilibrium state. Whilst this equation is probably strictly true of a gaseous system, its application to equilibria in liquid media may occasionally lead to erroneous results, for a slight displacement of the equilibrium may be associated with a slight change in the partial free energy of the liquid medium. The condition of equilibrium is thus more precisely given by

$$dF_A + dF_B + \dots + dF_P + dF_Q + \dots + dF_{\text{medium}} = 0 \quad (2)$$

for a small displacement. For equilibria involving neutral molecules this change in the partial free energy of the medium may usually be ignored, but for equilibria involving ions it may under certain circumstances be considerable, as it comprises 1/3rd of the net partial free electrical energy change of the ions caused by the slight displacement of the ionic equilibrium.

In order to demonstrate this result which follows directly from the Debye-Hückel theory¹ of strong electrolytes, the determination of the activity coefficient of an ion in terms of the valence of the ion and of the ionic strength μ , will first be considered. In Debye's evaluation of the total electrical free energy of an electrolyte solution² the ions are considered as initially uncharged so that if their concentration is c the free energy of the system in the uncharged state will be $F_0 + nkT \ln c/c_0$, where F_0 is the free energy of the system at the infinitely small concentration c_0 . The electrical work required to increase the charges of the ions reversibly to their final values is evaluated as $A_0 = \sum n_i z_i e \psi_i/3$, where z_i is the number of unit charges, e , possessed by the n ions of the i 'th kind considered and ψ_i is the potential at one of these ions due to the surrounding ion atmosphere. As was shown by Debye and Hückel (*loc. cit.*), $\psi_i = -z_i e \kappa/D$, κ being a quantity characteristic of the solution and defined by

$$\kappa^2 = \frac{4\pi}{DKT} \sum n_i z_i^2 e^2 = \frac{8\pi e^2 N\mu}{10^3 DKT}$$

¹ *Physik. Z.*, 24, 185 (1923).

² Debye: *Physik. Z.*, 25, 97 (1924).

The total free energy of the electrolyte solution is thus $F_0 + nkT \ln c/c_0 - n_1 z_1^2 e^2 \kappa / 3D$, or for a symmetrical binary electrolyte forming a total number of n ions

$$F = F_0 + nkT \ln c/c_0 - nz^2 e^2 \kappa / 3D \quad (3)$$

The free energy change measured in reversible concentration cells is the free energy of transfer of ions from one solution where their concentration is c_1 to another where their concentration is c_2 , i.e., the free energy change is the *partial* free energy change of the ions. In order to compare the activity coefficients of ions deduced from these measurements of partial free energy changes, with the theory, Debye calculated the partial free energy of the electrolyte by differentiating the total free energy of the solution with respect to n and so obtained the result

$$\bar{F} = nkT \ln c/c_0 - nz^2 e^2 \kappa / 2D \quad (4)$$

Part of the electrical free energy of the electrolyte solution must therefore reside in the medium since the total free electrical energy is $-nz^2 e^2 \kappa / 3D$, whilst the partial free electrical energy of the ions is $-nz^2 e^2 \kappa / 2D$. This leaves $+nz^2 e^2 / 6D$ as the partial free electrical energy of the medium.

Comparison of the partial free energy of the ions with the expression $\bar{F} = nkT \ln f c/c_0$, which defines the activity coefficient f in terms of the solution concentration c_0 of unit activity coefficient, shows that

$$\ln f = -nz^2 e^2 \kappa / 2DkT \quad (5)$$

or $\log f = -0.505 z^2 \sqrt{\mu}$ at 25° .

Conditions of equilibrium in a balanced reaction associated with a change in the partial free electrical energy.—As a simple example of a balanced reaction in which a change in the free electrical energy occurs, an equilibrium of the type $HA \rightleftharpoons H' + A'$, may be considered, where a weak acid HA ionises forming ions H' and A' . Let dn mols of HA ionise, forming dn ions each of H' and A' , and let c_{HA} , $c_{H'}$, and $c_{A'}$ be the various equilibrium concentrations. The free energy change of the system, dF , associated with this small displacement, will be $dF_{HA} + dF_{H'} + dF_{A'} + dF_{\text{medium}}$, and at equilibrium $dF = 0$. Thus

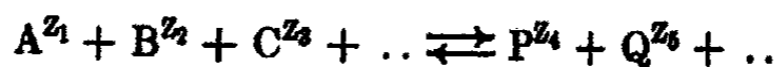
$$-dF_{HA} - \frac{dn}{N} RT \ln c_{HA} + dF_{H'} + \frac{dn}{N} RT \ln c_{H'} -$$

$$dnz^2 e^2 \kappa / 2D + dF_{A'} + \frac{dn}{N} RT \ln c_{A'} - dnz^2 e^2 \kappa / 2D + 2 \times dn z^2 e^2 \kappa / 6D = 0$$

and therefore

$$\ln \frac{c_{H'} c_{A'}}{c_{HA}} = \text{Const.} + \frac{2z^2 e^2 \kappa}{3DkT} \quad (6)$$

For an equilibrium of the type



$$\ln \frac{c_{P^{z_4}} c_{Q^{z_5}} \dots}{c_{A^{z_1}} c_{B^{z_2}} c_{C^{z_3}} \dots} = \text{const.} + \frac{e^2 \kappa}{3DkT} (z_4^2 + z_5^2 - (z_1^2 + z_2^2 + z_3^2)) \quad (7)$$

The activity equilibrium constant.—The activity of a molecular species A, may be defined by the equation, $F_A = RT \ln a_A + C_A$, where a_A is the activity and C_A is a constant. This definition leads to the activity equilibrium constant if (1) is valid. As has been indicated (1) is not applicable to ionic equilibria in which a displacement of the equilibrium is attended by a change in the free electrical energy of the system. An alternative procedure is to define activities by the activity equilibrium constant and so evaluate "apparent" activity coefficients. For the ionic equilibrium $HA \rightleftharpoons H' + A'$, this method would give

$$\frac{a_H a_{A'}}{a_{HA}} = \frac{c_H c_{A'}}{c_{HA}} \cdot \frac{f_H f_{A'}}{f_{HA}} = \text{Const.}$$

and since f_{HA} may be regarded as unity,

$$\ln \frac{c_H c_{A'}}{c_{HA}} = \ln \text{Const.} - 2 \ln f_1 \quad (8)$$

where f_1 is the activity coefficient of a univalent ion.

Comparison of equations (6) and (8) gives

$$\ln f_1 = z^2 e^2 \kappa / 3 D k T \quad (9)$$

or $\log f = -0.33 z^2 \sqrt{\mu}$ at 25° .

A similar result is obtained by application of the ionic velocity equation (previous paper) to the equilibrium $HA \rightleftharpoons H' + A'$. The rate of interaction of the ions is given by

$$v = k c_H c_{A'} e^{-E_0/kT + 1.52 \sqrt{\mu}} \quad (10)$$

whilst the rate of ionisation is given

$$v' = k' c_{HA} e^{-E_0'/kT} \quad (11)$$

At equilibrium $v = v'$, and

$$\frac{c_H c_{A'}}{c_{HA}} = \left(\frac{k' e^{-E_0'/kT}}{k e^{-E_0/kT}} \right) e^{-1.52 \sqrt{\mu}}$$

$$\text{or } \log \frac{c_H c_{A'}}{c_{HA}} = \log \text{Const.} - \frac{1.52}{2.303} \sqrt{\mu} \quad (12)$$

Comparison of equation (12) with (8), gives

$$\log f_1 = -0.33 \sqrt{\mu}$$

Activity coefficients evaluated from the definition of activity in terms of the partial free energy, $F_A = C_A + RT \ln a_A$; thus correspond to a limiting law of $\log f = -0.50 z^2 \sqrt{\mu}$, whilst activity coefficients evaluated from the equilibrium constant definition, $a_A a_B \dots a_P a_Q \dots K$, correspond to the limiting law $\log f = -0.33 z^2 \sqrt{\mu}$, when the equilibrium is such that neutral molecules are in equilibrium with ions. There are consequently two series of activity values which will in general differ from each other. It may be of interest to consider briefly to which series the various measurements of activity should be assigned.

¹ Lewis: Proc. Am. Acad., 43, 259 (1907); Z. physik. Chem., 61, 129, (1907).

Activities from solubility.—Since the calculation of activity coefficients from solubility measurements is based on the condition that the ionic activity product is constant, such activity coefficients should show agreement with the formula $\log f = -0.33 z^2 \sqrt{\mu}$. This result is obtained more directly by consideration of the free energy change attending the solution of a small quantity of salt in the saturated solution, remembering that each ion formed contributes $+z^2 e^2 k/6D$ to the partial free electrical energy of the medium. Brønsted found for univalent electrolytes¹ that the limiting law, $\log f = -0.42 z^2$, satisfied the solubility relationships. Later work,² however, has been in accordance with the expression $\log f = -0.50 z^2 \sqrt{\mu}$, but since when the ionic radii are taken into account the Debye equation becomes

$$\log f = \frac{-z^2 B \sqrt{\mu}}{1 + Aa \sqrt{\mu}}$$

where A and B are constants, B having the value 0.505 or 0.33, the evaluation of B from experimental data depends on the value assigned to a , the ionic radius.

The measurement of the partial vapour pressure of the electrolyte in the solution, as in the case of the halogen acids, may be considered as a solubility method and the activity coefficients obtained by this method correspond to the limiting law, $\log f = -0.33 z^2 v$. It must therefore follow that the vapour pressure of an electrolyte is not even approximately proportional to the fugacity,³ f' , as defined by $FA = RT \ln f' + CA$.

Activities from freezing points.—In the measurement of activities from the freezing point depression one obtains primarily the activity of the solvents in the solution. At the freezing point the activity of the solvent in the solution is equal to the activity of the solid solvent and the change in both these activities with temperature is calculable. In a solution at any desired temperature the activity of the solvent present is therefore known. The partial free energies of the solvent and the solute, F^1 and F^2 respectively, are connected by the equation⁴

$$N_1 \left(\frac{\partial F^1}{\partial N_1} \right) + N_2 \left(\frac{\partial F^2}{\partial N_1} \right) = 0$$

If one defines the activity by $F_2 = RT \ln a_2 + C_2$, then

$$N_1 \left(\frac{\partial a_1}{\partial N_1} \right) + N_2 \left(\frac{\partial a_2}{\partial N_1} \right) = 0$$

and one obtains from this equation the activity of the solute corresponding to the above definition and therefore to the limiting law for the activity coefficient $\log f = -0.50 z^2 \sqrt{\mu}$.

Summary

1. The equation for the equilibrium of electrolytes in solution has been modified to take into account the partial free electrical energy of the medium as deduced from the Debye-Hückel theory of electrolytic solutions.

¹ J. Am. Chem. Soc., 44, 938 (1922).

² Scatchard: J. Am. Chem. Soc., 47, 641 (1925).

³ Lewis: loc. cit.

⁴ Lewis and Randall: "Thermodynamics", 207 (1923).

2. It is shown that the two definitions of activity (1) in terms of the partial free energy $F_A = RT \ln a_A + C_A$, and (2) in terms of the equilibrium constant, $a_A a_B \dots / a_P a_Q \dots = K$, lead, when applied to electrolytes, to two series of values.

3. Activity coefficients evaluated from values for the activity of the solvent, e.g., from the freezing point depression, correspond to the Debye limiting law, $\log f = -0.50 z^2 \sqrt{\mu}$, whilst activity coefficients evaluated from solubility measurements or from the partial v. p. of the electrolyte correspond to the limiting law, $\log f = -0.33 z^2 \sqrt{\mu}$.

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June 11, 1937.*

THE SYSTEM $\text{Na}_2\text{O} : \text{SiO}_2 : \text{H}_2\text{O}$

Relationship between Composition and Boiling Point of Aqueous Solutions of Sodium Silicate. II*

BY JESSIE Y. CANN AND KEREN E. GILMORE¹

This investigation is a continuation of the research begun by Cann and Cheek² on the relationship between composition and boiling points of the system $\text{Na}_2\text{O} : \text{SiO}_2 : \text{H}_2\text{O}$ i.e. so-called aqueous solutions of sodium silicate. Because of the peculiar characteristics of silicate solutions, no work had been recorded upon this subject prior to 1925.

Apparatus and Materials

The apparatus used for all determinations in this work was the Cottrell³ boiling point apparatus, as modified by Washburn.⁴ With this it is possible to obtain a boiling point which varies only a few thousandths of a degree for a period of an hour or longer. The apparatus was made of Pyrex glass, since Cann and Cheek found that ordinary glass would not stand the necessary heat. Two similar pieces of apparatus were placed side by side on the laboratory desk and heated by burners of identical form, fed by the same gas supply, so that there was equal exposure to any slight fluctuation of atmospheric pressure, accidental draught, variation of gas pressure, etc. Each piece of apparatus was wrapped in asbestos paper, and surrounded by a box of heavy asbestos board.⁴ In one was placed conductivity water, and in the other the silicate solution. Pieces of clean unglazed porcelain were added to each to prevent bumping. The ground-glass stoppers of the apparatus in which the silicate solution was boiled were covered with tin foil to prevent possible cementing by an unavoidable trace of the silicate solution.

The silicates used in this investigation were the commercial brands "C", "K" "E" and "S" furnished by the Philadelphia Quartz Company. The ratio of soda to silica in these brands was found to be 1:1.99, 1:2.87, 1:3.15 and 1:3.75 respectively. "E" was clear, light in weight and very mobile. "S" was very much like "E" except that it was opalescent. "K" was much darker, slightly heavier and more viscous. "C" was transparent, heavy and exceedingly viscous, and most difficult to handle. The color was probably due to traces of iron found in analyses of each. These samples were kept in block-tin containers.

Conductivity water was used throughout the investigation.

*Contribution from the Chemistry Laboratory of Smith College.

¹ The experimental work of this paper was submitted by Keren E. Gilmore in partial fulfillment of the requirement for the degree of Master of Arts at Smith College.

² Ind. Eng. Chem., 17, 512 (1925).

³ J. Am. Chem. Soc., 41, 721 (1919).

⁴ Washburn and Read: J. Am. Chem. Soc., 41, 729 (1919).

Experimental Work

The solutions used for the determinations were prepared by adding silicate to water with brisk stirring.³ From the reputed soda content, solutions of varying approximate percentage composition were made up. Half a liter of each was prepared in order to provide sufficient material for the boiling point determinations to be made in duplicate. The solutions were then allowed to stand twenty-four hours in stoppered glass bottles, since it is a well known fact that the composition of freshly diluted silicate solutions varies during the first twelve or fifteen hours but that after this no change occurs. During the period that the dilute solutions were kept in the glass bottles no reaction took place between the solutions and the glass, for two determinations were in as close agreement when made a week apart as when made on the same day.

The volume of solution used for each determination depended upon the particular apparatus. It was found that the best results were obtained when the apparatus was about a third full, i.e. when the volume of the solution was about one hundred and fifty cubic centimeters. After the solution had been placed in one apparatus and conductivity water in the other, each was brought to boiling. When the Beckmann thermometer in each, after being gently tapped, showed, through the lens, that the readings were constant within a few thousandths of a degree, a succession of readings was recorded at two minute intervals. Immediately before and after each determination the barometric pressure and the temperature at the barometer were read. The barometer was on the same level as the apparatus. By the simultaneous use of these two pieces of apparatus any possible error caused by fluctuation in atmospheric conditions was reduced to a minimum.

Solutions made from "E" and "C" frothed badly. This frothing increased with increasing concentration. When the soda content exceeded three per cent the foam extended above the thermometer bulb, and, in some cases, completely filled the apparatus. An attempt was made to lessen the effect of the foam on the attainment of equilibrium by fastening a piece of perforated sheet platinum to the stem of the pumping apparatus about two inches above the liquid. This reduced the frothing somewhat, but did not prevent a portion of the foam from reaching the thermometer bulb.

It was impossible to determine the boiling-point elevation of silicate solutions which contained over eighteen per cent silica without injuring the apparatus. A white crystalline-like substance was deposited in the bottom of the apparatus which either softened the glass or cracked it. The Pyrex glass was easily forced out of shape by the weight of the solution. This behavior of Pyrex glass is not an unusual phenomenon. Morey⁵ attributes it to the high per cent of B_2O_3 and SiO_2 in the glass.

⁵ Private communication. "While Pyrex is a good glass to withstand acid solutions it is perhaps the poorest for alkalis. A Pyrex tube will be completely decomposed and all the B_2O_3 extracted by a few hours heating with water alone at 300°C , under which conditions most other glasses are but slightly affected. That ten per cent of B_2O_3 in Pyrex, taken in connection with eighty per cent of silica and the low content of basic oxides, makes it peculiarly susceptible to the action of strong alkalis."

The formation of this white substance is very characteristic. When the solution is first heated, a continuous stream of vapor bubbles arises from definite points on the bottom of the apparatus. As the heating continues the points grow in size and a white solid appears. The solid continues to form as long as the solution is heated. Throughout the process a large amount of water vapor separates. The greater part of the solid material goes back into solution when it is allowed to cool in contact with the supernatant liquid.

The authors separated some of this apparently crystalline material by slowly heating the stock solution of "E" in a round bottomed flask connected with a reflux condenser, and then filtering hot through a Buchner funnel. Stericker⁶ examined microscopically some of this white solid and found that it consisted of spherical shells with holes in one side from which the bubbles of water vapor arose. Morey⁷ made a more thorough microscopic study of the material. He powdered it, immersed it in a liquid of known refractive index, and tested its behavior in polarized light. All silicates are biaxial crystals and therefore show birefringence. The material examined has only one refractive index which indicates that it is a liquid and therefore belongs to the category of glasses. Morey⁸ affirms that it is very difficult to crystallize sodium silicate from an aqueous solution. If crystallization occurs the solution has to be free from such impurities as iron oxide and alumina, and heated under definitely prescribed conditions of temperature and composition. Thus if an aqueous solution of sodium silicate is heated rapidly a glass results.

The accurate soda content of all solutions was determined by titration with standard acid, using methyl orange as an indicator. The complete analysis of the original samples was carried out according to the accepted methods of Hillebrand.⁹

Results

Sixteen determinations of the boiling-point of conductivity water at different pressures were made with both Beckmann thermometers. The observed barometric pressures were corrected to 0°C for the expansion of mercury with temperature according to Landolt and Börnstein.⁹ The boiling points¹⁰ at these corrected pressures correspond exactly to the observed Beckmann readings. The average of these Beckmann readings, corrected to 760 m. m. pressure, correspond to 100°C. The reading on the thermometer used in the silicate apparatus, corresponding to the boiling point of water under standard conditions, is 0.0963° higher than the analogous reading of the thermometer used in the water apparatus.

⁶ Phila. Quartz Co.

⁷ Geophysical Laboratory.

⁸ U. S. Geol. Survey Bull. 422 (1910); 700 (1919).

⁹ Tabellen, p. 40 (1912).

¹⁰ Tabellen, p. 365 (1912).

TABLE I
Boiling Point Elevation of Silicate Solutions

| No. | Bar. Press. corrected to 0°C B mm. | Observed Beckmann reading of thermometer used for solution | Observed Beckmann reading of thermometer used for water | Corresponding Beckmann reading for water boiling under pressure B | Boiling-point elevation of solution at pressure B | Boiling-point elevation of solution at pressure 760 mm. | Soda content Per cent |
|-----|------------------------------------|------------------------------------------------------------|---------------------------------------------------------|-------------------------------------------------------------------|---------------------------------------------------|---------------------------------------------------------|-----------------------|
| "C" | | | | | | | |
| 4a | 752.410 | 1.1725 | 0.9491 | 1.0454 | 0.1271 | 0.1276 | 0.316 |
| 4b | 756.115 | 1.3001 | 1.0798 | 1.1761 | 0.1240 | 0.1243 | 0.316 |
| 1 | 756.482 | 1.3254 | 1.0725 | 1.1688 | 0.1566 | 0.1567 | 0.421 |
| 2a | 741.498 | 0.8791 | 0.5379 | 0.6342 | 0.2449 | 0.2463 | 0.946 |
| 2b | 759.784 | 1.5493 | 1.2077 | 1.3040 | 0.2453 | 0.2453 | 0.947 |
| 3a | 753.056 | 1.3213 | 0.9533 | 1.0496 | 0.2717 | 0.2723 | 1.136 |
| 3b | 763.895 | 1.7132 | 1.3635 | 1.4598 | 0.2534 | 0.2531 | 1.170* |
| 5a | 741.397 | 1.0258 | 0.5375 | 0.6338 | 0.3920 | 0.3936 | 1.933 |
| 5b | 755.970 | 1.5502 | 1.0725 | 1.1688 | 0.3814 | 0.3819 | 1.888 |
| 6 | 764.980 | 2.2443 | 1.4135 | 1.5098 | 0.7345 | 0.7334 | 4.874 |
| 7a | 768.331 | 2.6769 | 1.5197 | 1.6160 | 1.0609 | 1.0578 | 7.486 |
| 7b | 768.063 | 2.6756 | 1.5049 | 1.6012 | 1.0744 | 1.0721 | 7.508† |
| 8a | 759.950 | 2.6690 | 1.2110 | 1.3073 | 1.3617 | 1.3617 | 9.516‡ |
| 8b | 757.890 | 2.5798 | 1.1364 | 1.2327 | 1.3471 | 1.3480 | 9.540 |

*Uneven pumping in silicate apparatus due to insufficient heat.

†Uneven pumping in water apparatus.

‡Uneven pumping in silicate apparatus probably due to viscosity of solution.

"K"

| | | | | | | | |
|----|---------|--------|--------|--------|--------|--------|-------|
| 9 | 753.711 | 1.1417 | 0.9816 | 1.0779 | 0.0638 | 0.0639 | 0.109 |
| 10 | 756.289 | 1.2662 | 1.0707 | 1.1670 | 0.0992 | 0.0993 | 0.223 |
| 1 | 762.325 | 1.5015 | 1.2822 | 1.3785 | 0.1230 | 0.1230 | 0.495 |
| 2 | 755.063 | 1.2965 | 1.0261 | 1.1224 | 0.1741 | 0.1743 | 0.809 |
| 3a | 759.728 | 1.5084 | 1.1849 | 1.2812 | 0.2272 | 0.2272 | 1.241 |
| 3b | 754.093 | 1.3076 | 0.9871 | 1.0834 | 0.2242 | 0.2246 | 1.253 |
| 4a | 761.130 | 1.6902 | 1.2313 | 1.3276 | 0.3626 | 0.3625 | 2.472 |
| 4b | 761.414 | 1.7088 | 1.2574 | 1.3537 | 0.3551 | 0.3550 | 2.466 |
| 5a | 765.059 | 2.0240 | 1.4749 | 1.5712 | 0.4528 | 0.4529 | 3.550 |
| 5b | 759.085 | 1.7316 | 1.1775 | 1.2738 | 0.4578 | 0.4579 | 3.502 |
| 6a | 764.603 | 2.0203 | 1.3871 | 1.4834 | 0.5369 | 0.5361 | 4.511 |
| 6b | 779.279 | 2.5384 | 1.8955 | 1.9918 | 0.5466 | 0.5434 | 4.416 |
| 7a | 755.635 | 1.8046 | 1.0236 | 1.1199 | 0.6847 | 0.6856 | 5.942 |
| 7b | 754.979 | 1.8214 | 1.0396 | 1.1359 | 0.6855 | 0.6865 | 5.982 |
| 11 | 763.123 | 2.2690 | 1.3325 | 1.4288 | 0.8402 | 0.8394 | 7.456 |
| 8 | 755.840 | 2.1105 | 1.0495 | 1.1458 | 0.9647 | 0.9659 | 8.638 |

TABLE I (Continued)
Boiling Point Elevation of Silicate Solutions

| No. | Ba. Press. corrected to 0°C B mm. | Observed Beckmann reading of thermometer used for solution | Observed Beckmann reading of thermometer used for water | Correspond- ing Beck- mann read- ing for water boiling under pres- sure B | Boiling point eleva- tion of solution at pressure B | Boiling point eleva- tion of solution at pressure 760 mm. | Soda content Per cent |
|-----|-----------------------------------------------|---------------------------------------------------------------------------|------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|--------------------------------------------------------------------|--------------------------------------------------------------------------|-----------------------------|
| "E" | | | | | | | |
| 1a | 757.708 | 1.2696 | 1.1026 | 1.1989 | 0.0707 | 0.0707 | 0.307† |
| 1b | 765.503 | 1.5473 | 1.3883 | 1.4846 | 0.0627 | 0.0627 | 0.309† |
| 2a | 759.276 | 1.3377 | 1.1343 | 1.2306 | 0.1071 | 0.1071 | 0.611† |
| 2b | 751.787 | 1.1074 | 0.8907 | 0.9870 | 0.1204 | 0.1207 | 0.637† |
| 3a | 744.287 | 0.9171 | 0.6257 | 0.7220 | 0.1951 | 0.1960 | 1.122 |
| 3b | 769.501 | 1.8227 | 1.5357 | 1.6320 | 0.1907 | 0.1902 | 1.122 |
| 4a | 769.196 | 1.9244 | 1.5245 | 1.6208 | 0.3036 | 0.3027 | 2.433 |
| 4b | 759.577 | 1.5803 | 1.1789 | 1.2752 | 0.3051 | 0.3051 | 2.455 |
| 5a | 766.012 | 1.9210 | 1.4118 | 1.5081 | 0.4129 | 0.4122 | 3.553† |
| 5b | 765.033 | 1.8730 | 1.3858 | 1.4821 | 0.3909 | 0.3905 | 3.553† |
| 6a | 752.578 | 1.5365 | 0.9331 | 1.0294 | 0.5071 | 0.5082 | 4.783† |
| 6b | 757.987 | 1.7133 | 1.0990 | 1.1953 | 0.5180 | 0.5183 | 4.706† |
| 7 | 744.915 | 1.3338 | 0.6431 | 0.7394 | 0.5944 | 0.5970 | 5.467† |

†Per cent by volume.

‡Large amount of frothing occurred.

"G"

| | | | | | | | |
|----|---------|--------|--------|--------|--------|--------|--------|
| 1a | 750.033 | 1.0552 | 0.8579 | 0.9542 | 0.1010 | 0.1013 | 0.143 |
| 1b | 753.333 | 1.1779 | 0.9881 | 1.0844 | 0.0935 | 0.0937 | 0.143 |
| 2a | 764.730 | 1.6435 | 1.3980 | 1.4943 | 0.1492 | 0.1490 | 0.498 |
| 2b | 762.515 | 1.5692 | 1.3099 | 1.4062 | 0.1630 | 0.1629 | 0.497† |
| 3a | 758.180 | 1.4629 | 1.1681 | 1.2644 | 0.1985 | 0.1986 | 0.762 |
| 3b | 756.015 | 1.3749 | 1.0856 | 1.1819 | 0.1930 | 0.1932 | 0.778 |
| 4a | 761.794 | 1.6502 | 1.2710 | 1.3673 | 0.2829 | 0.2828 | 1.512 |
| 4b | 761.725 | 1.6479 | 1.2681 | 1.3644 | 0.2835 | 0.2834 | 1.495 |
| 5a | 763.982 | 1.8121 | 1.3493 | 1.4456 | 0.3665 | 0.3664 | 2.571 |
| 5b | 764.081 | 1.7812 | 1.3116 | 1.4079 | 0.3733 | 0.3730 | 2.572 |
| 6 | 761.153 | 1.7480 | 1.2293 | 1.3256 | 0.4224 | 0.4223 | 3.479 |
| 7 | 754.747 | 1.6229 | 1.0197 | 1.1160 | 0.5069 | 0.5067 | 4.577 |

†Used new apparatus for water which did not pump well.

In Table I are given the boiling point elevations of the silicate solutions at 760 m.m. pressure, and the percentage soda content of the solutions. The figures in the second column represent the barometric pressure corrected to 0°C .⁹ The figures in the fifth column are obtained by adding 0.0963 to those in the fourth column. The figures in the sixth column are the differences between those in the third and the fifth. The figures in the seventh column were calculated according to Washburn and Read.¹¹

TABLE II
Analysis of Original Samples

| Soln. | Na_2O | SiO_2 | Fe_2O_3 | (Per cent.) | CaO | MgO | H_2O | Fe |
|------------|-----------------------|----------------|-------------------------|-------------------------|--------------|--------------|----------------------|-------------|
| | | | | Al_2O_3 | | | | |
| "C" | | | | | | | | |
| 1 | 17.986 | 35.752 | 0.124 | 0.304 | 0.038 | 0.061 | | 0.086 |
| 2 | 17.967 | 35.802 | 0.134 | 0.305 | 0.033 | 0.016 | | 0.093 |
| Av. | 17.977 | 35.777 | 0.129 | 0.304 | 0.035 | 0.038 | 45.740 | 0.089 |
| "K" | | | | | | | | |
| 1 | 11.157 | 32.072 | 0.138 | 0.587 | 0.121 | 0.024 | | 0.096 |
| 2 | 11.163 | 32.068 | 0.076 | 0.679 | 0.051 | 0.012 | | 0.053 |
| Av. | 11.160 | 32.070 | 0.107 | 0.633 | 0.086 | 0.018 | 45.926 | 0.074 |
| "E" | | | | | | | | |
| 1 | 8.997 | 28.224 | 0.146 | 0.368 | 0.031 | 0.000 | | 0.102 |
| 2 | 8.904 | 28.227 | | | 0.023 | 0.000 | | |
| Av. | 8.950 | 28.225 | 0.146 | 0.368 | 0.027 | 0.000 | 62.284 | 0.102 |
| "S" | | | | | | | | |
| 1 | 6.896 | 25.882 | 0.022 | 0.217* | 0.030 | 0.000 | | 0.015 |
| 2 | 6.892 | 25.865 | 0.038 | 0.237 | 0.035 | 0.000 | | 0.026 |
| Av. | 6.894 | 25.873 | 0.030 | 0.227 | 0.032 | 0.000 | 66.944 | 0.020 |

*The high Al_2O_3 values are evidently due to traces of other elements (Ti, etc.) for which tests were not made.

Table II gives the complete analyses of the original silicate solutions, and Table III gives the complete analyses and calculated formulas of all the solutions of "C", "K", "E" and "S" that were used.

¹¹ J. Am. Chem. Soc., 41, 738 (1919).

TABLE III
Complete Analyses and Formulas of All Solutions used

| No. | Na ₂ O | SiO ₂ | Fe ₂ O ₃ | Per cent. | | | H ₂ O | Ratio of H ₂ O to Na ₂ O: SiO ₂ 1.99 |
|-------|-------------------|------------------|--------------------------------|--------------------------------|-------|-------|------------------|-----------------------------------------------------------------------------|
| | | | | "C" | | | | |
| | | | | Al ₂ O ₃ | CaO | MgO | | |
| 4a | 0.316 | 0.629 | 0.002 | 0.005 | 0.000 | 0.000 | 99.048 | 1078.65 |
| 4b | 0.316 | 0.629 | 0.002 | 0.005 | 0.000 | 0.000 | 99.048 | 1078.65 |
| 1 | 0.421 | 0.838 | 0.003 | 0.007 | 0.000 | 0.000 | 98.731 | 807.06 |
| 2a | 0.946 | 1.887 | 0.007 | 0.016 | 0.002 | 0.002 | 97.140 | 353.38 |
| 2b | 0.947 | 1.885 | 0.007 | 0.016 | 0.002 | 0.002 | 97.141 | 353.01 |
| 3a | 1.136 | 2.261 | 0.008 | 0.019 | 0.002 | 0.002 | 96.572 | 292.55 |
| 3b | 1.170 | 2.329 | 0.008 | 0.020 | 0.002 | 0.002 | 96.469 | 283.75 |
| 5a | 1.933 | 3.847 | 0.014 | 0.033 | 0.004 | 0.004 | 94.165 | 167.65 |
| 5b | 1.888 | 3.757 | 0.014 | 0.032 | 0.004 | 0.004 | 94.301 | 171.89 |
| 6 | 4.874 | 9.700 | 0.035 | 0.082 | 0.009 | 0.010 | 85.300 | 60.23 |
| 7a | 7.486 | 14.898 | 0.054 | 0.127 | 0.015 | 0.016 | 77.404 | 35.58 |
| 7b | 7.508 | 14.942 | 0.054 | 0.127 | 0.015 | 0.016 | 77.338 | 35.50 |
| 8a | 9.516 | 18.939 | 0.068 | 0.161 | 0.018 | 0.021 | 71.297 | 25.78 |
| 8b | 9.540 | 18.986 | 0.069 | 0.161 | 0.018 | 0.021 | 71.205 | 25.69 |
| Orig. | 17.977 | 35.777 | 0.129 | 0.304 | 0.035 | 0.038 | 45.740 | 8.76 |

TABLE III (continued)
Complete Analyses and Formulas of All Solutions used

| No. | Na ₂ O | SiO ₂ | Fe ₂ O ₃ | Per cent. | | | H ₂ O | Ratio of H ₂ O to Na ₂ O: SiO ₂ 2.874 |
|-------|-------------------|------------------|--------------------------------|--------------------------------|-------|-------|------------------|------------------------------------------------------------------------------|
| | | | | "K" | | | | |
| | | | | Al ₂ O ₃ | CaO | MgO | | |
| 9 | 0.109 | 0.313 | 0.001 | 0.006 | 0.000 | 0.000 | 99.571 | 3143.69 |
| 10 | 0.223 | 0.641 | 0.002 | 0.012 | 0.002 | 0.000 | 99.118 | 1529.63 |
| 1 | 0.495 | 1.423 | 0.005 | 0.028 | 0.003 | 0.000 | 98.046 | 681.65 |
| 2 | 0.809 | 2.325 | 0.008 | 0.058 | 0.006 | 0.001 | 96.793 | 411.75 |
| 3a | 1.241 | 3.565 | 0.012 | 0.070 | 0.009 | 0.002 | 95.101 | 263.73 |
| 3b | 1.253 | 3.601 | 0.012 | 0.071 | 0.010 | 0.002 | 95.051 | 261.06 |
| 4a | 2.472 | 7.106 | 0.024 | 0.140 | 0.019 | 0.004 | 90.235 | 125.57 |
| 4b | 2.466 | 7.086 | 0.024 | 0.139 | 0.019 | 0.004 | 90.262 | 125.97 |
| 5a | 3.550 | 10.204 | 0.034 | 0.201 | 0.027 | 0.005 | 85.980 | 83.35 |
| 5b | 3.502 | 10.004 | 0.034 | 0.199 | 0.027 | 0.006 | 86.228 | 84.74 |
| 6a | 4.511 | 12.963 | 0.043 | 0.256 | 0.035 | 0.007 | 82.186 | 62.70 |
| 6b | 4.416 | 12.986 | 0.042 | 0.251 | 0.034 | 0.007 | 82.264 | 64.11 |
| 7a | 5.942 | 17.075 | 0.057 | 0.345 | 0.045 | 0.009 | 76.528 | 44.32 |
| 7b | 5.982 | 17.190 | 0.057 | 0.339 | 0.046 | 0.010 | 76.376 | 43.94 |
| 11 | 7.456 | 21.426 | 0.072 | 0.423 | 0.057 | 0.012 | 70.556 | 31.83 |
| 8 | 8.638 | 24.823 | 0.083 | 0.490 | 0.066 | 0.014 | 65.888 | 26.25 |
| Orig. | 11.160 | 32.070 | 0.107 | 0.633 | 0.086 | 0.018 | 45.926 | 14.16 |

TABLE III (Continued)
Complete Analyses and Formulas of All Solutions used

| No. | Na_2O | SiO_2 | Per cent. | | | | MgO | H_2O | Ratio of H_2O to Na_2O : SiO_2 3.154 |
|-------|-----------------------|----------------|-------------------------|-------------------------|--------------|----------------------|--------------|----------------------|-------------------------------------------------------------------------------------|
| | | | Fe_2O_3 | Al_2O_3 | CaO | H_2O | | | |
| | | | | "E" | | | | | |
| 1a | 0.307 | 0.968 | 0.005 | 0.012 | 0.000 | none | 98.708 | 1106.49 | |
| 1b | 0.309 | 0.975 | 0.005 | 0.013 | 0.000 | " | 98.698 | 1099.22 | |
| 2a | 0.611 | 1.927 | 0.009 | 0.025 | 0.001 | " | 97.427 | 548.75 | |
| 2b | 0.637 | 2.009 | 0.010 | 0.026 | 0.001 | " | 97.317 | 525.76 | |
| 3a | 1.122 | 3.538 | 0.018 | 0.046 | 0.003 | " | 95.273 | 292.22 | |
| 3b | 1.122 | 3.538 | 0.018 | 0.046 | 0.003 | " | 95.273 | 292.22 | |
| 4a | 2.433 | 7.673 | 0.040 | 0.100 | 0.005 | " | 89.749 | 126.95 | |
| 4b | 2.455 | 7.742 | 0.040 | 0.101 | 0.005 | " | 89.657 | 125.68 | |
| 5a | 3.553 | 11.205 | 0.058 | 0.146 | 0.010 | " | 85.028 | 82.36 | |
| 5b | 3.553 | 11.205 | 0.058 | 0.146 | 0.010 | " | 85.028 | 82.36 | |
| 6a | 4.783 | 15.084 | 0.078 | 0.197 | 0.014 | " | 79.844 | 57.45 | |
| 6b | 4.706 | 14.841 | 0.077 | 0.194 | 0.014 | " | 80.167 | 58.62 | |
| 7 | 5.467 | 17.241 | 0.089 | 0.225 | 0.016 | " | 76.962 | 48.45 | |
| Orig. | 8.950 | 28.225 | 0.146 | 0.368 | 0.027 | " | 62.284 | 23.95 | |

TABLE III (Continued)
Complete Analyses and Formulas of All Solutions used

| No. | Na_2O | SiO_2 | Per cent. | | | | MgO | H_2O | Ratio of H_2O to Na_2O : SiO_2 3.753 |
|-------|-----------------------|----------------|-------------------------|-------------------------|--------------|----------------------|--------------|----------------------|-------------------------------------------------------------------------------------|
| | | | Fe_2O_3 | Al_2O_3 | CaO | H_2O | | | |
| | | | | "S" | | | | | |
| 1a | 0.143 | 0.536 | 0.000 | 0.004 | 0.000 | none | 99.317 | 2390.13 | |
| 1b | 0.143 | 0.536 | 0.000 | 0.004 | 0.000 | " | 99.317 | 2390.13 | |
| 2a | 0.498 | 1.869 | 0.002 | 0.016 | 0.002 | " | 97.613 | 674.55 | |
| 2b | 0.497 | 1.865 | 0.002 | 0.016 | 0.002 | " | 97.618 | 675.94 | |
| 3a | 0.762 | 2.859 | 0.003 | 0.025 | 0.003 | " | 96.348 | 435.24 | |
| 3b | 0.778 | 2.919 | 0.003 | 0.026 | 0.003 | " | 96.271 | 425.84 | |
| 4a | 1.512 | 5.674 | 0.006 | 0.049 | 0.007 | " | 92.752 | 211.11 | |
| 4b | 1.495 | 5.611 | 0.007 | 0.049 | 0.007 | " | 92.831 | 213.69 | |
| 5a | 2.571 | 9.649 | 0.011 | 0.084 | 0.012 | " | 87.673 | 117.35 | |
| 5b | 2.572 | 9.653 | 0.011 | 0.085 | 0.012 | " | 87.667 | 117.30 | |
| 6 | 3.479 | 13.056 | 0.015 | 0.114 | 0.016 | " | 83.320 | 82.42 | |
| 7 | 4.577 | 17.178 | 0.019 | 0.150 | 0.021 | " | 78.055 | 55.69 | |
| Orig. | 6.894 | 25.873 | 0.030 | 0.227 | 0.032 | " | 66.944 | 33.42 | |

It will be noticed that in calculating the formulas, the percentages of the impurities—i.e. Fe_2O_3 , Al_2O_3 , CaO and MgO —are ignored. This has been done because it is believed that these percentages are so small as to be negligible.

TABLE IV--(a)
Activity Coefficients—"C"

| Ratio of H ₂ O to Na ₂ O: SiO ₂ 1.99 | $\frac{0.00025}{\nu} \int_0^m \frac{\theta}{m} d\theta$ (negligible); $\int_0^{0.01} -j d \log m = 0.0005 \left\{ \begin{array}{l} \alpha = 1.396 \\ \beta = 0.938 \end{array} \right.$ | $\log m$ | $j = 1 - \frac{\theta}{\lambda m}$ | $\log j$ | $\int_0^m j d \log m$ | $\frac{j}{2.303}$ | $-\log \gamma$ | γ |
|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|------------------------------------|----------|-----------------------|-------------------|----------------|----------|
| 1078.65 | 0.0515 | 2.7114 | -0.1968 | | 0.2292 | -0.0855 | 0.1437 | 0.7182 |
| 1078.65 | 0.0515 | 2.7114 | -0.1659 | | 0.2292 | -0.0722 | 0.1570 | 0.6966 |
| 807.06 | 0.0688 | 2.8374 | -0.0996 | | 0.3164 | -0.0433 | 0.2731 | 0.5332 |
| 353.38 | 0.1571 | 1.1961 | 0.2432 | 1.3860 | 0.6484 | 0.1056 | 0.7540 | 0.1762 |
| 353.01 | 0.1572 | 1.1966 | 0.2471 | 1.3928 | 0.6484 | 0.1073 | 0.7557 | 0.1755 |
| 292.55 | 0.1897 | 1.2781 | 0.3074 | 1.4876 | 0.7380 | 0.1335 | 0.8715 | 0.1345 |
| 283.75 | 0.1956 | 1.2914 | 0.3756 | 1.5747 | 0.7580 | 0.1631 | 0.9211 | 0.1199 |
| 167.65 | 0.3311 | 1.5199 | 0.4263 | 1.6297 | 1.0208 | 0.1851 | 1.2059 | 0.0623 |
| 171.89 | 0.3229 | 1.5091 | 0.4292 | 1.6327 | 1.0361 | 0.1864 | 1.2225 | 0.0599 |
| 60.23 | 0.9216 | 1.9645 | 0.6159 | 1.7895 | 1.6723 | 0.2675 | 1.9398 | 0.0115 |
| 35.58 | 1.5600 | 0.1931 | 0.6728 | 1.8279 | 2.0157 | 0.2921 | 2.3078 | 0.0049 |
| 35.50 | 1.5036 | 0.1941 | 0.6691 | 1.8255 | 2.0157 | 0.2905 | 2.3062 | 0.0049 |
| 25.78 | 2.1531 | 0.3331 | 0.6948 | 1.8418 | 2.2230 | 0.3017 | 2.5247 | 0.0030 |
| 25.69 | 2.1606 | 0.3346 | 0.6989 | 1.8444 | 2.2230 | 0.3035 | 2.5265 | 0.0030 |

TABLE IV—(b)
Activity Coefficients—"K"

$$\frac{0.00025}{\nu} \int_0^m \frac{\theta}{m} d\theta = 0.000014 \text{ (negligible); } \int_0^{0.01} -j d \log m = 0.002 \begin{cases} \alpha = 1.175 \\ \beta = 1.202 \end{cases}$$

| Ratio of H ₂ O to Na ₂ O: SiO ₂ : 2.874 | m | $\log m$ | $j = 1 - \frac{\theta}{\nu \Delta m}$ | $\log j$ | $\int_0^m j d \log m$ | $\frac{j}{2.303}$ | $\frac{\theta}{m}$ | θ | $-\log \gamma$ | γ |
|--------------------------------------------------------------------------------|--------|----------|---------------------------------------|----------|-----------------------|-------------------|--------------------|----------|----------------|----------|
| 681.65 | 0.0814 | 2.9108 | 0.2710 | 1.4330 | 0.2112 | 0.1177 | 1.5105 | 0.1230 | 0.3289 | 0.4690 |
| 411.75 | 0.1348 | 1.1297 | 0.3760 | 1.5752 | 0.3235 | 0.1633 | 1.2931 | 0.1743 | 0.4868 | 0.3260 |
| 263.73 | 0.2105 | 1.3232 | 0.4790 | 1.6803 | 0.4456 | 0.2080 | 1.0795 | 0.2272 | 0.6536 | 0.2220 |
| 261.06 | 0.2126 | 1.3276 | 0.4902 | 1.6904 | 0.4483 | 0.2129 | 1.0564 | 0.2246 | 0.6612 | 0.2182 |
| 125.57 | 0.4420 | 1.6455 | 0.6042 | 1.7812 | 0.6785 | 0.2624 | 0.8201 | 0.3625 | 0.9409 | 0.1146 |
| 125.97 | 0.4407 | 1.6442 | 0.6022 | 1.7797 | 0.6785 | 0.2615 | 0.8055 | 0.3550 | 0.9400 | 0.1148 |
| 83.35 | 0.6659 | 1.8234 | 0.6718 | 1.8272 | 0.8251 | 0.2917 | 0.6661 | 0.4529 | 1.1168 | 0.0764 |
| 84.74 | 0.6550 | 1.8163 | 0.6626 | 1.8213 | 0.8320 | 0.2877 | 0.6991 | 0.4579 | 1.1197 | 0.0759 |
| 62.70 | 0.8853 | 1.9471 | 0.7077 | 1.8499 | 0.9307 | 0.3073 | 0.6056 | 0.5361 | 1.2380 | 0.0578 |
| 64.11 | 0.8658 | 1.9374 | 0.6971 | 1.8433 | 0.9415 | 0.3027 | 0.6276 | 0.5434 | 1.2442 | 0.0570 |
| 44.32 | 1.2524 | 0.0977 | 0.7358 | 1.8668 | 1.0766 | 0.3195 | 0.5474 | 0.6856 | 1.3961 | 0.0402 |
| 43.94 | 1.2633 | 0.1015 | 0.7377 | 1.8679 | 1.0803 | 0.3203 | 0.5434 | 0.6865 | 1.4006 | 0.0398 |
| 31.83 | 1.7438 | 0.2415 | 0.7677 | 1.8852 | 1.2130 | 0.3334 | 0.4814 | 0.8394 | 1.5464 | 0.0284 |
| 26.25 | 2.1146 | 0.3252 | 0.7795 | 1.8918 | 1.2866 | 0.3385 | 0.4568 | 0.9659 | 1.6251 | 0.0237 |
| 3143.69 | 0.0177 | 2.2469 | -0.7467 | | | | | 0.0639 | | |
| 1529.63 | 0.0363 | 2.5598 | -0.3207 | | | | | 0.0993 | | |

TABLE IV—(c)
Activity Coefficients—"E"

| Ratio of H ₂ O to Na ₂ O: SiO ₂ 3.154 | $\frac{0.00025}{\nu} \int_0^m \frac{\theta}{m} d\theta$ (negligible); $\int_0^{0.01} -j d \log m = 0.0428 \begin{cases} \alpha = 0.585 \\ \beta = 0.851 \end{cases}$ | | | | | | | |
|------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|----------------------------------------|----------|-----------------------|-------------------|----------------|----------|
| | m | $\log m$ | $j = 1 - \frac{\theta}{\nu \lambda m}$ | $\log j$ | $\int_0^m j d \log m$ | $\frac{j}{2.303}$ | $-\log \gamma$ | γ |
| 1106.49 | 0.0502 | 2.7004 | 0.3198 | 1.5049 | 0.1250 | 0.1389 | 0.2639 | 0.5447 |
| 1099.22 | 0.0505 | 2.7033 | 0.4007 | 1.6029 | 0.1261 | 0.1740 | 0.3001 | 0.5011 |
| 548.75 | 0.1012 | 1.0050 | 0.4890 | 1.6893 | 0.2367 | 0.2123 | 0.4490 | 0.3556 |
| 525.76 | 0.1056 | 1.0236 | 0.4482 | 1.6515 | 0.2444 | 0.1946 | 0.4390 | 0.3639 |
| 292.22 | 0.1900 | 1.2786 | 0.5020 | 1.7007 | 0.3544 | 0.2180 | 0.5724 | 0.2677 |
| 292.22 | 0.1900 | 1.2786 | 0.5107 | 1.7133 | 0.3544 | 0.2244 | 0.5788 | 0.2638 |
| 126.95 | 0.4372 | 1.6407 | 0.6659 | 1.8234 | 0.5562 | 0.2891 | 0.8453 | 0.1428 |
| 125.68 | 0.4417 | 1.6451 | 0.6666 | 1.8239 | 0.5612 | 0.2895 | 0.8507 | 0.1411 |
| 82.36 | 0.6740 | 1.8286 | 0.7048 | 1.8481 | 0.6778 | 0.3061 | 0.9839 | 0.1038 |
| 82.36 | 0.6740 | 1.8286 | 0.7204 | 1.8576 | 0.6778 | 0.3128 | 0.9906 | 0.1022 |
| 57.45 | 0.9662 | 1.9851 | 0.7461 | 1.8728 | 0.7787 | 0.3240 | 1.1027 | 0.0789 |
| 58.62 | 0.9469 | 1.9763 | 0.7358 | 1.8668 | 0.7843 | 0.3195 | 1.1038 | 0.0787 |
| 48.45 | 1.1456 | 0.0591 | 0.7485 | 1.8742 | 0.8378 | 0.3250 | 1.1628 | 0.0687 |

TABLE IV—(d)
Activity Coefficients—"S"

$$\frac{0.00025}{\gamma} \int_0^m \frac{\theta}{m} d\theta \text{ (negligible); } \int_0^{0.01} -j d \log m = 0.0004 \begin{cases} \alpha = 1.203 \\ \beta = 0.968 \end{cases}$$

| Ratio of H ₂ O to Na ₂ O: SiO ₂ 3.753 | m | $\log m$ | $j = 1 - \frac{\theta}{\gamma \Delta m}$ | $\log j$ | $\int_0^m j d \log m$ | $\frac{j}{2.303}$ | $-\log \gamma$ | γ |
|------------------------------------------------------------------------------|--------|----------|------------------------------------------|----------|-----------------------|-------------------|----------------|----------|
| 674.55 | 0.0823 | 2.9153 | 0.1261 | 1.1007 | 0.2847 | 0.0548 | 0.3395 | 0.4577 |
| 675.94 | 0.0821 | 2.9144 | [0.0426] | [2.6293] | 0.2847 | 0.0185 | 0.3032 | 0.4975 |
| 435.24 | 0.1275 | 1.1056 | 0.2484 | 1.3952 | 0.4143 | 0.1079 | 0.5222 | 0.3005 |
| 425.84 | 0.1303 | 1.1151 | 0.2846 | 1.4543 | 0.4234 | 0.1236 | 0.5470 | 0.2838 |
| 211.11 | 0.2629 | 1.4198 | 0.4809 | 1.6820 | 0.6833 | 0.2088 | 0.8921 | 0.1282 |
| 213.69 | 0.2598 | 1.4146 | 0.4734 | 1.6753 | 0.6872 | 0.2056 | 0.8928 | 0.1280 |
| 117.35 | 0.4730 | 1.6749 | 0.6261 | 1.7967 | 0.9513 | 0.2719 | 1.2232 | 0.0598 |
| 117.30 | 0.4732 | 1.6750 | 0.6196 | 1.7921 | 0.9558 | 0.2690 | 1.2248 | 0.0596 |
| 82.42 | 0.6735 | 1.8283 | 0.6974 | 1.8435 | 1.1273 | 0.3028 | 1.4301 | 0.0372 |
| 55.69 | 0.9967 | 1.9986 | 0.7546 | 1.8777 | 1.3364 | 0.3277 | 1.6641 | 0.0217 |
| 2390.13 | 0.0232 | 2.3659 | [-1.1052] | | | | | |
| 2390.13 | 0.0232 | 2.3659 | [-0.9473] | | | | | |

TABLE IV—(e)
Activity Coefficients—"BW"

| Ratio of H ₂ O to Na ₂ O: SiO ₂ 1.68 | $\frac{0.00025}{\gamma} \int_0^m \frac{\theta}{m} (d\theta) \text{ (negligible); } \int_0^{0.01} -j d \log m = 0.1738 \left\{ \begin{array}{l} \alpha = 0.327 \\ \beta = 0.589 \end{array} \right.$ | | | | | | | |
|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|-----------------------------------|----------|-----------------------|-------------------|----------------|----------|
| | m | $\log m$ | $j = 1 - \frac{\theta}{\gamma m}$ | $\log j$ | $\int_0^m j d \log m$ | $\frac{j}{2.303}$ | $-\log \gamma$ | γ |
| 610.43 | 0.0909 | 2.9586 | 0.5434 | 1.7351 | 0.2963 | 0.2360 | 0.5323 | 0.2936 |
| 493.82 | 0.1124 | 1.0508 | 0.4675 | 1.6698 | 0.3118 | 0.2030 | 0.5148 | 0.3056 |
| 477.13 | 0.1163 | 1.0657 | 0.8963 | 1.9524 | 0.3153 | 0.3892 | 0.7045 | 0.1975 |
| 409.26 | 0.1356 | 1.1323 | 0.4306 | 1.6341 | 0.3276 | 0.1870 | 0.5146 | 0.3058 |
| 374.90 | 0.1481 | 1.1704 | 0.7620 | 1.8820 | 0.3353 | 0.3309 | 0.6662 | 0.2157 |
| 360.03 | 0.1538 | 1.1870 | 0.5701 | 1.7560 | 0.3384 | 0.2476 | 0.5860 | 0.2595 |
| 319.94 | 0.1735 | 1.2393 | 0.6078 | 1.7837 | 0.3481 | 0.2639 | 0.6120 | 0.2444 |
| 303.79 | 0.1827 | 1.2618 | 0.4996 | 1.6986 | 0.3531 | 0.2169 | 0.5700 | 0.2691 |
| 276.92 | 0.2005 | 1.3020 | 0.3788 | 1.5784 | 0.3616 | 0.1645 | 0.5261 | 0.2978 |
| 172.09 | 0.3226 | 1.5087 | 0.4839 | 1.6848 | 0.4107 | 0.2101 | 0.6208 | 0.2394 |
| 105.18 | 0.5277 | 1.7224 | 0.5473 | 1.7382 | 0.4624 | 0.2377 | 0.7001 | 0.1995 |
| 76.03 | 0.7301 | 1.8634 | 0.5518 | 1.7418 | 0.5117 | 0.2396 | 0.7513 | 0.1773 |
| 53.48 | 1.0403 | 0.0172 | 0.6126 | 1.7872 | 0.5613 | 0.2660 | 0.8273 | 0.1488 |
| 42.54 | 1.3048 | 0.1155 | 0.6335 | 1.8017 | 0.5971 | 0.2751 | 0.8722 | 0.1342 |
| 31.80 | 1.7450 | 0.2418 | 0.6491 | 1.8123 | 0.6427 | 0.2818 | 0.9245 | 0.1190 |
| 26.06 | 2.1395 | 0.3283 | 0.6657 | 1.8233 | 0.6765 | 0.2891 | 0.9656 | 0.1083 |

TABLE IV—(f)
Activity Coefficients—"Star"

$$\frac{0.00025}{p} \int_0^m \frac{\theta}{m} d\theta \text{ (negligible); } \int_0^{0.01} -j d \log m = 0.1105 \begin{cases} \alpha = 0.405 \\ \beta = 0.664 \end{cases}$$

| Ratio of H_2O to $\text{Na}_2\text{O}:$ SiO_2 2.55 | m | $\log m$ | $j = 1 - \frac{\theta}{pNm}$ | $\log j$ | $\int_0^m j d \log m$ | $\frac{j}{2.303}$ | $-\log j$ | γ |
|-----------------------------------------------------------------------------------|--------|----------|------------------------------|----------|-----------------------|-------------------|-----------|----------|
| 711.28 | 0.0780 | 2.8923 | 0.4001 | 1.6022 | 0.1141 | 0.1737 | 0.2878 | 0.5154 |
| 393.44 | 0.1411 | 1.1495 | 0.3945 | 1.5960 | 0.1816 | 0.1713 | 0.3529 | 0.4437 |
| 308.60 | 0.1799 | 1.2550 | 0.4660 | 1.6684 | 0.2160 | 0.2024 | 0.4184 | 0.3816 |
| 223.33 | 0.2485 | 1.3954 | 0.5417 | 1.7338 | 0.2731 | 0.2352 | 0.5083 | 0.3102 |
| 30.61 | 1.8134 | 0.2585 | 0.7727 | 1.8880 | 0.6960 | 0.3355 | 1.0315 | 0.0930 |
| 34.64 | 1.6024 | 0.2048 | 0.7298 | 1.8632 | 0.6060 | 0.3169 | 0.9229 | 0.1194 |
| 29.37 | 1.8899 | 0.2764 | 0.7543 | 1.8775 | 0.7082 | 0.3275 | 1.0357 | 0.0921 |

In Table IV are given the activity coefficients of all the solutions whose boiling points were determined. These values were calculated according to the equations for concentrated solutions given by Lewis and Randall.¹² First, the molality i.e. the grams of $(\text{Na}_2\text{O})_1$, $(\text{SiO}_2)_x$ in 1000 grams of water was calculated for each. These values are listed in the second column. Then the

values of $j = 1 - \frac{\theta}{\nu\lambda m}$ where θ = the elevation of the boiling point, ν the

number of ions at infinite dilution, λ the molecular elevation of water i.e. 0.518 and m the molality, were calculated. These values are given in the fourth column. The value of ν was assumed to be 4, because it was desired to compare the results obtained from boiling point elevation with those obtained by Harman¹³ in all of his recently published work on silicates. Especially was it desired to compare the present results with those obtained by Harman by the freezing-point method.¹⁴ He used the value of 4 for ν to represent the four ions 2Na^+ , SiO_3^- , OH^- . Moreover it is stated by Lewis and Randall¹⁵ that it is possible to use the same equations for boiling point elevation as for freezing point depression.

Log j was next plotted against log m and the intercept ($\log \beta$) on the log j axis was determined, and the slope of the line, α . From these two values

the $\int_0^{0.01} -j d \log m$ was obtained from equation 15, namely $\int_0^{0.01} -j d \log m = -\frac{\beta}{2.303\alpha} (0.01)^\alpha$. This gives the area from infinite dilution up to molality =

0.01. Then j was plotted against log m , and the curves extrapolated until they cut the axis log $m = -2$. To obtain the values of the activity coefficients

according to the equation $\log \gamma = \int_0^m -j d \log m - \frac{j}{2.303} + \frac{0.00025}{\nu} \int_0^m \frac{\theta}{m} d\theta$

given by Lewis and Randall, it is necessary, in order to determine the values

of $\int_0^m -j d \log m$, to obtain the area under the curve of j against log m . To

the areas, corresponding to each molality, counted to the right of the point where log $m = -2$, must be added the value of the area corresponding to

$\int_0^{0.01} -j d \log m$ obtained from equation 15. These values are listed in the

sixth column of Table IV.

The value of $\frac{0.00025}{\nu} \int_0^m \frac{\theta}{m} d\theta$ was determined for solutions of "K" only,

because its value was found to be entirely negligible.

¹² Lewis and Randall: "Thermodynamics," pp. 342, 346, 347 (1923).

¹³ J. Phys. Chem., 29, 1155 (1925); 30, 359, 917, 1100 (1926); 31, 355, 511 (1927).

¹⁴ J. Phys. Chem., 31, 355 (1927).

¹⁵ Loc. cit.

¹⁶ Lewis and Randall: loc. cit., p. 346.

Table IV also includes the activity coefficients calculated for the results on "BW" and "Star" obtained by Cann and Cheek.²

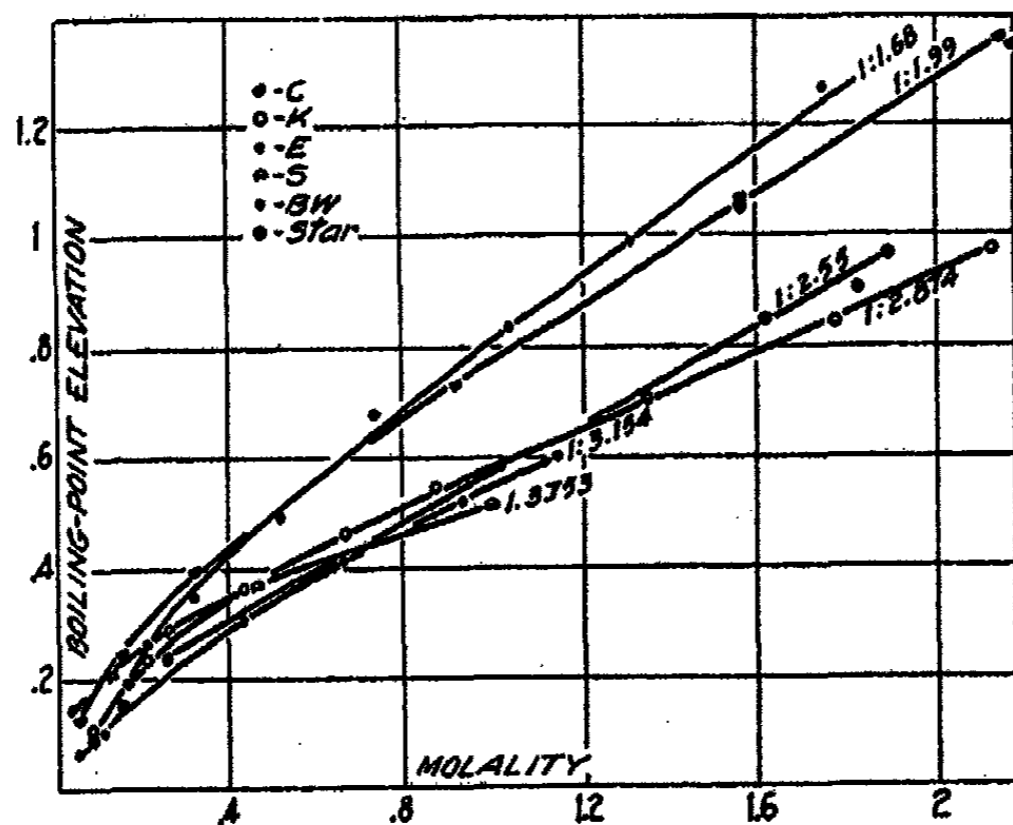


FIG. 1 shows graphically the relationship between the boiling point elevations and the molalities of all the solutions used.

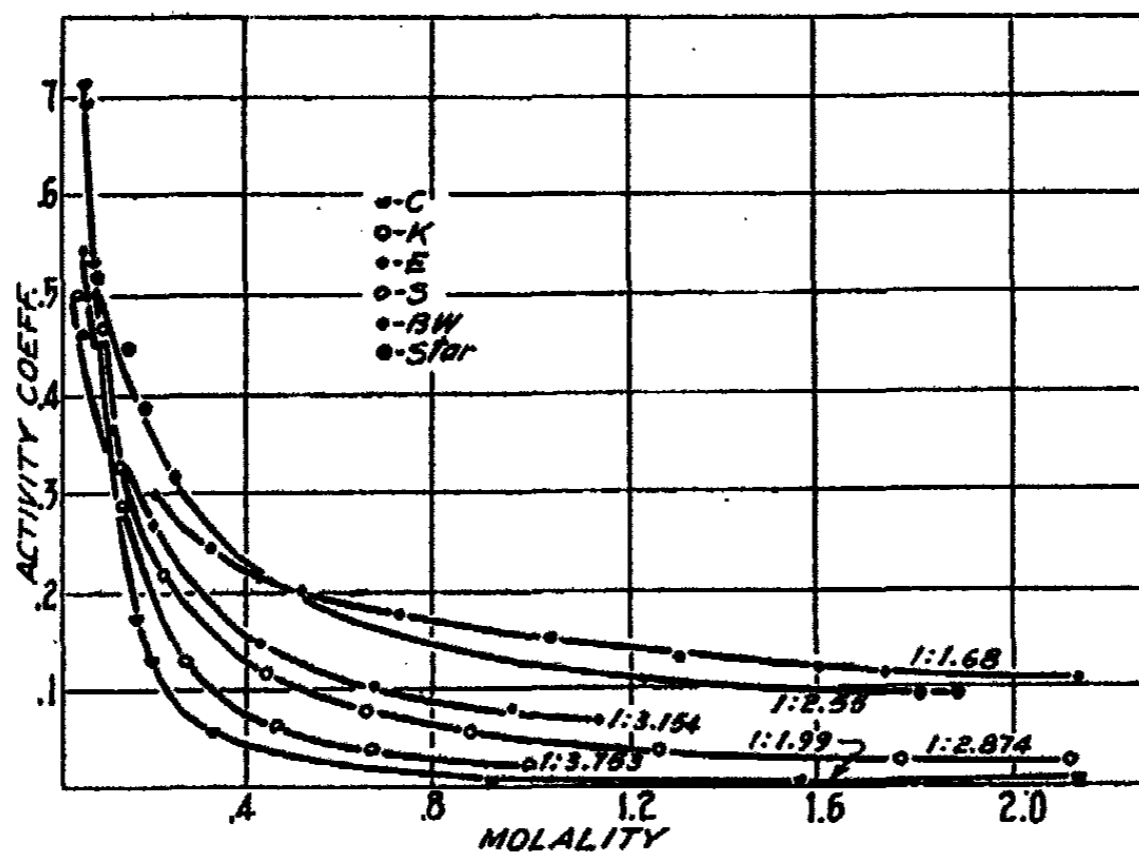


FIG. 2 shows graphically the relationship between the activity coefficients and the molalities of all the solutions used.

TABLE V
Molality and Activity Coefficients for the ratios

| Molality | Na ₂ O : SiO ₂ | | | | | |
|----------|--------------------------------------|--------------------|----------|--------------------|------------------|--------------------|
| | 1 : 1.68 | 1 : 1.995 | 1 : 2.55 | 1 : 2.874 | 1 : 3.154 | 1 : 3.753 |
| 0.05 | | { 0.6966 0.7182 | | | 0.5447 0.5011 | |
| 0.07 | | 0.5332 | | | | |
| 0.08 | | | 0.5154 | 0.4690 | | 0.4577 |
| 0.09 | 0.2936 | | | | | 0.4975 |
| 0.10 | | | | | 0.3556 | |
| 0.11 | 0.3056 | | | | | |
| 0.12 | 0.1975 | | | | | |
| 0.14 | 0.3058 | | 0.4437 | 0.3260 | | { 0.3005 0.2838 |
| 0.15 | { 0.2157 0.2595 | | | | | |
| 0.16 | | { 0.1762 0.1755 | | | | |
| 0.17 | 0.2444 | | | | | |
| 0.18 | 0.2691 | | 0.3816 | | | |
| 0.19 | | 0.1345 | | | | |
| 0.20 | 0.2978 | 0.1199 | | | 0.2677 | |
| 0.21 | | | | 0.2220 | | |
| 0.25 | | | 0.3102 | | | |
| 0.26 | | | | | | 0.1282 |
| 0.32 | 0.2394 | 0.0599 | | | | |
| 0.33 | | 0.0623 | | | | |
| 0.44 | | | | { 0.1148 0.1146 | 0.1428 0.1411 | |
| 0.47 | | | | | | 0.0598 |
| 0.53 | 0.1995 | | | { 0.0759 0.0764 | | |
| 0.66 | | | | | 0.1038 | 0.0372 |
| 0.67 | | | | | | |
| 0.73 | 0.1773 | | | | | |
| 0.88 | | | | 0.0578 | | |
| 0.92 | | 0.0115 | | | | |
| 0.96 | | | | | 0.0789 | 0.0217 |
| 1.04 | 0.1488 | | | | | |
| 1.14 | | | | | 0.0687 | |
| 1.25 | | | | 0.0402 | | |
| 1.26 | | | | 0.0398 | | |
| 1.30 | 0.1342 | | | | | |
| 1.56 | | 0.0049 | | | | |
| 1.60 | | | 0.1194 | | | |
| 1.75 | 0.1190 | | | 0.0284 | | |
| 1.81 | | | 0.0930 | 0.0237 | | |
| 1.89 | | | 0.0921 | | | |
| 2.13 | 0.1083 | | | | | |
| 2.16 | | 0.0030 | | | | |

Table V is a summation of all the results showing the activity coefficients of all the ratios for the same molalities.

Discussion of Results

The results of this investigation are, for the most part, in agreement with those of Harman.¹⁵ The curves in Fig. 1 show that concentrated solutions have proportionately less effect on the boiling point elevation than dilute solutions i.e. as concentration increases the percentage elevation in boiling point decreases. It is therefore believed that the degree of dissociation of solute decreases as concentration increases. Since the curves of "BW" (1:1.68) and "C" (1:1.99) have the greatest slope, it is evident that concentrated solutions which have a relatively small percentage of silica produce the greatest effect on the boiling point. For this reason the degree of dissociation is believed to be greater in solutions in which the ratio of soda to silica is low. It will be noticed that the slope of "S" (1:3.753) is different from that of any other curve. The boiling point elevation is exceptionally high in the dilute solutions and abnormally low in the concentrated solutions. Harman observed an analogous result from the freezing point depression of the 1:4 ratio. He attributes this result to micelle formation, which undoubtedly exists in this ratio.¹⁷

The curves in Fig. 2 for "BW" (1:1.68), "Star" (1:2.55), "K" (1:2.874) and "S" (1:3.753) agree with the foregoing statements. It will be noticed that "E" (1:3.154) and "C" (1:1.995) do not agree entirely with these statements. It will be recalled that solutions of "E" and "C" gave trouble because of frothing and so-called crystal formation.

It will also be noticed that in "C", only, have the three *negative* values of j been included. Two *negative* values of j for "K" and two for "S" have been omitted. The reason for this is that the omitted values for "K" and "S" were considered unreliable because of the extreme dilution. This was not considered true of the "C" values; although, if these three values for "C" in extremely dilute solution were discarded, the results would be more nearly concordant. Moreover, according to LaMer,¹⁸ from a thorough study of the best data in the literature, very slight experimental errors render j almost indeterminate in very dilute solutions. There is also the possibility that ν may not be equal to 4 in these dilutions. La Mer¹⁸ states "the silicate complexes in "C", dissociating as a weak electrolyte at the very high dilutions, may give more ions."

It had been thought that a decided change might take place in the composition of silicate solutions on prolonged heating. But results obtained by plotting time against elevation of boiling point, taken at two minute intervals, indicated no appreciable change during boiling.

¹⁷ J. Phys. Chem., 31, 373 (1927).

¹⁸ Victor K. LaMer: Columbia Univ. Private Communication.

Summary

1. The boiling point elevations of sodium silicate solutions of ratios 1:1.995, 1:2.874, 1:3.154 and 1:3.753 at various concentrations have been measured.
2. The values of the boiling point elevations have been plotted against the molalities.
3. The values of the activity coefficients have been calculated and plotted against the molalities.
4. The results of Cann and Cheek on ratios 1:1.68 and 1:2.55 have been treated similarly and added for comparison.
5. The results show that the degree of dissociation of solute decreases as concentration increases.
6. The boiling point elevations of dilute solutions of the ratio 1:3.753 are abnormally high while the elevations of the concentrated solutions are abnormally low, thus indicating micelle formation in this ratio.

A STUDY OF THE ACTIVITY AND FREE ENERGY OF DILUTION OF SOME SALTS OF CADMIUM

BY FREDERICK H. GETMAN

Although the activity coefficients of many typical electrolytes in both dilute and concentrated aqueous solutions have been determined, relatively few measurements have been recorded for the salts of cadmium. Apparently the only reliable data on the activity of cadmium salts are to be found in the experimental work of Horsch¹ on solutions of cadmium chloride and in the tables of activity coefficients of electrolytes compiled by Lewis and Randall.²

Owing to the fact that all of the salts of cadmium are somewhat anomalous in their behavior as electrolytes, it is highly desirable that their activity coefficients should be determined. With a view to supplying this data, the experimental work recorded in the present paper was undertaken. The salts which have thus far been studied are the chloride, bromide and sulphate of cadmium. Subsequently we hope to publish the results of studies now in progress on the activity of cadmium iodide.

Materials and Solutions

Cadmium Chloride. Chemically pure cadmium chloride was recrystallized, first from pure distilled water, and then from conductivity water. A determination of the water of crystallization in a sample of the dry salt showed it to contain 19.77% of water, while the theoretical content of water in $\text{CdCl}_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}$ is 19.72%.

Cadmium Bromide. A sample of chemically pure cadmium bromide was subjected to a similar process of recrystallization, but no attempt was made to confirm its purity by analysis.

Cadmium Sulphate. Chemically pure cadmium sulphate, $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$, suitable for the preparation of Weston cells, was subjected to a single recrystallization before using.

Mercury and Mercury Salts. All of the mercury used for electrodes, or for the preparation of amalgams, was of a very high order of purity, having been supplied through the courtesy of the Eppley Laboratories. Through the kindness of the same organization, samples of both electrolytic mercurous chloride and mercurous sulphate were obtained. The mercurous bromide which served as a depolarizer in the cadmium bromide cells was obtained from Kahlbaum and was certified to be chemically pure. Before setting up the bromide cells, the mercurous bromide used was shaken with the electrolyte in the presence of several globules of pure mercury.

Precautions were taken to protect all of the mercury salts from the action of light, both before and after assembling the cells.

¹ Horsch: J. Am. Chem. Soc., 41, 1787 (1919).

² Lewis and Randall: "Thermodynamics," 344, 362 (1923).

Cadmium. The cadmium employed in the preparation of the amalgams was also obtained from Kahlbaum and was guaranteed to be of a high order of purity. A stick of this metal also served as the anode of an electrolytic cell in which crystalline cadmium was deposited on spirals of platinum wire which subsequently were employed as negative electrodes in the experimental cells.

Solutions. All solutions were prepared with conductivity water. The concentrations of the stock solutions were determined gravimetrically, the chlorides and bromides being weighed as the corresponding silver halides and the sulphates as barium sulphate. The densities of the stock solutions were employed to express all concentrations in mols per 1000 grams of solvent.

Amalgams. All of the amalgams were prepared by direct weighing and contained 10% of cadmium. In the preparation of the amalgams the usual precautions were observed to prevent oxidation.

Apparatus

The measurements of electromotive force were carried out with a Leeds and Northrup Type K potentiometer in conjunction with a Type R galvanometer of high sensitivity manufactured by the same concern. Two independent standards of reference were employed, viz., (1) a Weston standard cell the electromotive force of which had recently been certified by the U. S. Bureau of Standards to be 1.01816 volts at 25.5 °C, and (2) an Eppley standard cell of the unsaturated Weston type the electromotive force of which was certified by the maker to be 1.01896 volt at 20°C. The cells were immersed in an electrically heated and controlled bath maintained at 25°C. and regulated to 0.01°. Temperatures were read on a thermometer which had been compared with a laboratory standard thermometer. The cells employed were either of the familiar H-form, or were made from large test-tubes provided with suitable sealed-in platinum connections.

Experimental

The following cells have been studied in this investigation:

- (1) Cd - CdCl₂(M) - Hg₂Cl₂ - Hg,
- (2) Cd - CdBr₂(M) - Hg₂Br₂ - Hg,
- and (3) Cd - CdSO₄(M) - Hg₂SO₄ - Hg.

The cadmium electrodes consisted either of 10% cadmium amalgams, or of pure electrolytic cadmium deposited on spirals of platinum wire from a solution of chemically pure cadmium sulphate to which a few drops of concentrated sulphuric acid had been added. A current of one milliamperere was allowed to flow through the cell for two hours, thus insuring a deposit of approximately four milligrams of crystalline cadmium. Cadmium electrodes prepared in this manner, on immersion in a solution of a cadmium salt at 25°C., have been found¹ gradually to acquire a potential corresponding to that of the modification of the metal known as α -cadmium which Cohen

¹ Getman: J. Am. Chem. Soc., 39, 1806 (1917).

and others¹ have shown to be stable at ordinary temperatures. The average value of the electromotive force of a 10% cadmium amalgam against pure α -cadmium at 25° was found to be 0.04742 volt, thus confirming the results of the earlier investigations to which reference has just been made. The electromotive forces of all cells in which the negative electrodes consisted of 10% cadmium amalgams were therefore increased by 0.04742 volt in order to obtain the value of the electromotive force referred to the pure metal.

In Tables I-III are given the measured values of the electromotive forces of cells in which the electrolytes were the chloride, bromide and sulphate of cadmium respectively.

TABLE I
Electromotive Force of Cadmium Chloride Cells

| Conc. (Mols per 1000 gm. H ₂ O) | E. M. F. volts | Conc. (Mols per 1000 gm. H ₂ O) | E. M. F. volts |
|--------------------------------------------------|-------------------|--------------------------------------------------|-------------------|
| 6.591* | 0.71822** | 0.0622 | 0.80632 |
| 5.909 | 0.72862 | 0.0311 | 0.81978 |
| 5.454 | 0.73020 | 0.0164 | 0.83247 |
| 5.035 | 0.73110 | 0.0086 | 0.84850 |
| 0.3113 | 0.77523 | 0.0062 | 0.8727 |
| 0.1556 | 0.78658 | 0.0031 | 0.8667 |
| 0.0819 | 0.80140 | 0.00086 | 0.9155 |

*Saturated solution.

**Lipscomb and Hulett's data.

TABLE II
Electromotive Force of Cadmium Bromide Cells

| Conc. (Mols per 1000 gm. H ₂ O) | E. M. F. volts | Conc. (Mols per 1000 gm. H ₂ O) | E. M. F. volts |
|--------------------------------------------------|-------------------|--------------------------------------------------|-------------------|
| 4.192* | 0.60000** | 0.0732 | 0.68054 |
| 3.1594 | 0.60506 | 0.0476 | 0.69147 |
| 0.4756 | 0.64524 | 0.0293 | 0.69928 |
| 0.2929 | 0.65507 | 0.0117 | 0.72023 |
| 0.1877 | 0.66400 | 0.0048 | 0.73678 |
| 0.1172 | 0.67331 | 0.0029 | 0.75071 |
| | | 0.0012 | 0.76240 |

*Saturated solution.

**Oehlm's data.

¹ Cohen and Helderman: Z. physik. Chem, 87, 409 (1914).; Hulett: Trans. Am. Electrochem. Soc., 7, 353 (1905); Getman: loc. cit.; Cohen: "Physico-Chemical Metamorphosis," 45 (1926).

TABLE III
Electromotive Force of Cadmium Sulphate Cells

| Conc. (Mols per 1000 gm. H ₂ O) | E. M. F. volts | Conc. (Mols per 1000 gm. H ₂ O) | E. M. F. volts |
|--------------------------------------------------|-------------------|--------------------------------------------------|-------------------|
| 3.698* | 1.06558 | 0.1386 | 1.11525 |
| 2.656 | 1.07681 | 0.1328 | 1.11782 |
| 2.125 | 1.08095 | 0.0554 | 1.12850 |
| 1.386 | 1.09259 | 0.0139 | 1.13988 |
| 0.5542 | 1.10335 | 0.0055 | 1.14840 |
| 0.2217 | 1.11298 | 0.0014 | 1.14381 |

*Saturated solution.

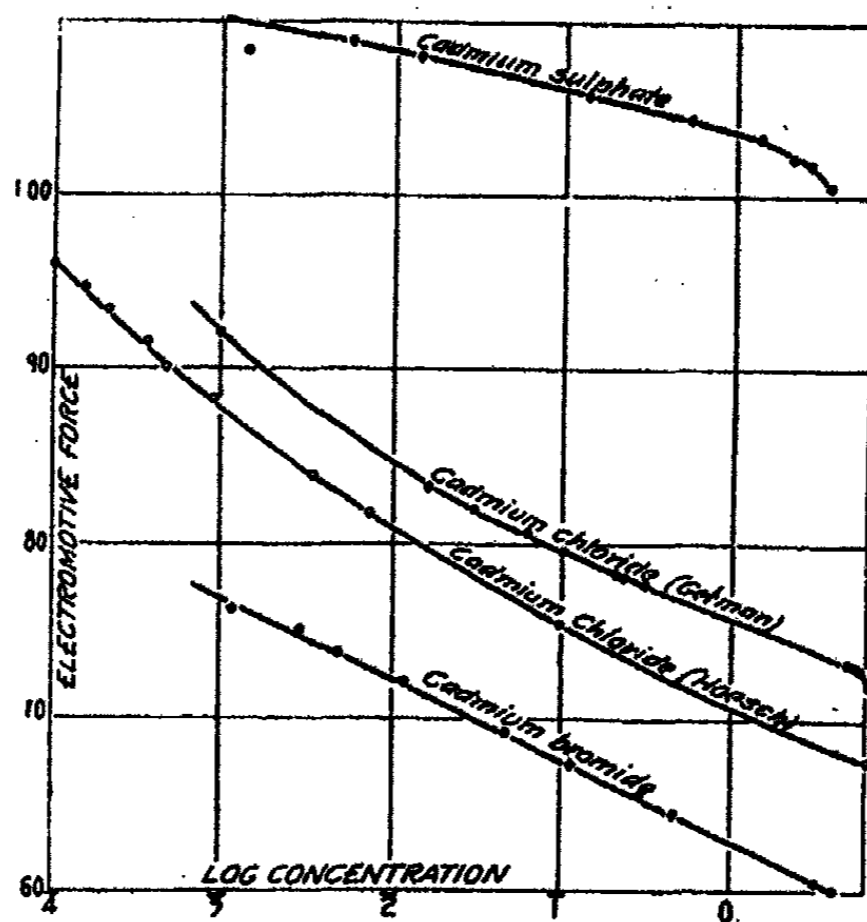


FIG. 1

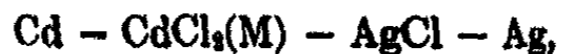
The data of the foregoing tables is represented graphically in Fig. 1. The four points on the curve for cadmium chloride which are designated by filled-in circles correspond to the saturated and nearly saturated solutions of the salt, and represent the experimental data obtained by Lipscomb and Hulett¹ in their studies of the calomel cell.

Similarly, the value for the electromotive force of the cell containing the saturated solution of cadmium bromide, and also designated by a filled-in circle, represents the results of Oeholm's² investigation of cadmium bromide

¹ Lipscomb and Hulett: J. Am. Chem. Soc., 38, 20 (1916).

² Oeholm: Chem. Zentr., 1, 1853 (1913).

cells. The data obtained by Horsch¹ with cells set up according to the scheme,



are reproduced in Fig. 1 for the sake of comparison with the data presented for cells in which mercury-mercurous chloride electrodes replace the silver-silver chloride electrodes employed by Horsch.

The values of the electromotive force of each of the cells tabulated above represent the average of a number of measurements extending over periods of time ranging from two to four days according to the stability of the cells. Precautions were taken to insure agreement of the individual electrodes amongst themselves; all cells which exhibited signs of instability were excluded.

With increasing dilution of the electrolytes, the electromotive force of the cells tended to fall off rapidly with time. This was especially noticeable in the cadmium sulphate cells where mercurous sulphate was used as a depolarizer. This behavior is probably due in part to increasing solubility of the depolarizer as the electrolyte becomes more dilute, and in the case of mercurous sulphate, is undoubtedly to be ascribed to the formation of a yellow basic mercurous sulphate which, according to Gouy² has the formula,



Evidence of the formation of this salt was obtained during the washing of the mercurous sulphate with the cell electrolyte in order to free the former from the sulphuric acid under which it was preserved. With all solutions of cadmium sulphate under 0.01 molal a distinct yellow coloration was observed on the surface of the depolarizer after several washings, the phenomenon becoming more pronounced as the electrolyte was diluted.

Before we can proceed to the calculation of the activity coefficients of the three salts, it is necessary to determine the potentials of the three positive electrodes in terms of the hydrogen electrode.

According to Lewis, Brighton and Sebastian³ the electromotive force of the cell,



is 0.5105 volt at 25°C. Taking the activity coefficient of HCl (0.01M) as 0.924, we have

$$E^\circ = 0.5105 + 0.05915 \log (0.01 \times 0.924),$$

or $E^\circ = 0.2702$ volt..

The electromotive force of the Hg-Hg₂Br₂ electrode referred to the hydrogen electrode has recently been determined by Gerke and Geddes⁴. The electromotive force of the cell,



¹ Horsch: loc. cit.

² Gouy: Compt. rend., 130, 1400 (1900).

³ Lewis, Brighton and Sebastian: J. Chem. Soc., 39, 2257 (1917).

⁴ Gerke and Geddes: J. Phys. Chem., 31, 886 (1927).

was found to be 0.2685 volt at 25°C. The activity coefficient of HBr (0.1M) may be taken as 0.814, hence

$$E^{\circ} = 0.2685 + 0.1183 \log (0.1 \times 0.814),$$

or $E^{\circ} = 0.1396$ volt.

In like manner, the Hg-Hg₂SO₄ electrode has been thoroughly investigated by both Lewis and Lacy¹ and Randall and Cushman.²

The electromotive force of the cell,



as determined by the above authors is 0.7444 volt at 25°C.

Taking 0.394 as the value of the activity coefficient of H₂SO₄ (0.0596M) we have

$$E^{\circ} = 0.7544 + 0.08873 \log (1.588 \times 0.506 \times 0.394),$$

or $E^{\circ} = 0.6213$ volt.

Calculation of the Activity Coefficients

In computing the values of the activity coefficients of solutions of the bi-univalent electrolytes, CdCl₂ and CdBr₂, we make use of the equation,

$$E = E^{\circ} - \frac{RT}{nF} \ln (4 m^2 \gamma^2),$$

while in calculating the activity coefficients of solutions of CdSO₄, we employ the corresponding equation for bi-bivalent electrolytes, viz.,

$$E = E^{\circ} - \frac{RT}{nF} \ln (M\gamma).$$

TABLE IV

Activity Coefficients of Solutions of Cadmium Chloride

| m | E' | E | γ | $\gamma(L \& R)$ | $\alpha(18^{\circ})$ |
|-------|--------|--------|----------|------------------|----------------------|
| 6.60 | 0.7182 | 0.4480 | 0.026 | 0.025 | |
| 1.0 | 0.7590 | 0.4888 | 0.059 | | |
| 0.5 | 0.7707 | 0.5005 | 0.093 | | 0.217 |
| 0.2 | 0.7860 | 0.5158 | 0.147 | | 0.293 |
| 0.1 | 0.7980 | 0.5278 | 0.21 | 0.219 | 0.375 |
| 0.05 | 0.8103 | 0.5401 | 0.31 | 0.30 | 0.453 |
| 0.02 | 0.8283 | 0.5581 | 0.49 | 0.44 | 0.584 |
| 0.01 | 0.8447 | 0.5745 | 0.64 | 0.532 | 0.664 |
| 0.005 | 0.8645 | 0.5943 | 0.76 | | 0.735 |
| 0.002 | 0.8950 | 0.6248 | 0.86 | | 0.818 |
| 0.001 | 0.9207 | 0.6505 | 0.89 | | 0.891 |

¹ Lewis and Lacy: J. Am. Chem. Soc., 36, 804 (1914).

² Randall and Cushman: J. Am. Chem. Soc., 40, 393 (1918).

Accepting as the normal electrode potential of cadmium at 25°C, $E^\circ = 0.3976$, the value determined by Horsch,¹ the above equations become, on passing to common logarithms,

$$E = E^\circ - 0.08873 \log (1.588 m\gamma),$$

and
$$E = E^\circ - 0.5915 \log (m\gamma).$$

The values of the activity coefficients given in Tables IV-VI have been calculated by substituting the smoothed values of the electromotive force, as read from the curves in Fig. 1, (referred to the hydrogen electrode) in the foregoing equations and solving for γ .

TABLE V
Activity Coefficients of Solutions of Cadmium Bromide

| m | E' | E | γ | $\alpha(18^\circ)$ | $\gamma(\text{calc})$ |
|-------|--------|--------|----------|--------------------|-----------------------|
| 4.19 | 0.6000 | 0.4604 | 0.029 | | |
| 1.0 | 0.6293 | 0.4897 | 0.06 | | |
| 0.5 | 0.6433 | 0.5037 | 0.08 | | |
| 0.2 | 0.6625 | 0.5229 | 0.12 | 0.200 | 0.10 |
| 0.1 | 0.6765 | 0.5369 | 0.17 | 0.286 | 0.17 |
| 0.05 | 0.6908 | 0.5512 | 0.23 | 0.370 | 0.24 |
| 0.02 | 0.7091 | 0.5695 | 0.36 | 0.486 | 0.37 |
| 0.01 | 0.7235 | 0.5839 | 0.50 | 0.572 | 0.55 |
| 0.005 | 0.7375 | 0.5979 | 0.65 | 0.660 | 0.67 |
| 0.002 | 0.7670 | 0.6274 | 0.81 | 0.778 | 0.81 |
| 0.001 | 0.7920 | 0.6524 | 0.85 | 0.852 | 0.85 |

TABLE VI
Activity Coefficients of Solutions of Cadmium Sulphate

| m | E' | E | γ | $\alpha(18^\circ)$ | $\gamma(\text{calc})$ |
|------|--------|--------|----------|--------------------|-----------------------|
| 3.70 | 1.0656 | 0.4443 | 0.04 | | |
| 1.0 | 1.0950 | 0.4737 | 0.05 | | |
| 0.5 | 1.1032 | 0.4819 | 0.08 | 0.245 | 0.11 |
| 0.2 | 1.1128 | 0.4915 | 0.13 | 0.290 | 0.15 |
| 0.1 | 1.1200 | 0.5087 | 0.20 | 0.332 | 0.21 |
| 0.05 | 1.1277 | 0.5064 | 0.29 | 0.377 | 0.26 |
| 0.02 | 1.1373 | 0.5160 | | 0.460 | 0.38 |
| 0.01 | 1.1447 | 0.5234 | | 0.534 | 0.51 |

In the foregoing tables E' denotes the smoothed values of electromotive force of the cells as read directly from the curves, while E denotes the electromotive force referred to the hydrogen electrode. In the fifth column of Table IV are given the activity coefficients of solutions of cadmium chloride as computed by Lewis and Randall² from the measurements of Horsch. In the sixth

¹ Horsch, loc. cit.

² Lewis and Randall: "Thermodynamics," 362 (1923).

column of Table IV and in the fifth columns of Tables V and VI are given the corresponding values of the conductance ratio, α , at 18°C., as computed by Noyes and Falk.¹ The sixth columns of Tables V and VI contain approximate values of the activity coefficients, estimated in the following manner:

$$\alpha_{\text{CdCl}_2} : \alpha_{\text{CdBr}_2} \text{ (or } \alpha_{\text{CdSO}_4}) = \gamma_{\text{CdCl}_2} \text{ (from Table I)} : \gamma_{\text{CdBr}_2} \text{ (or } \gamma_{\text{CdSO}_4})$$

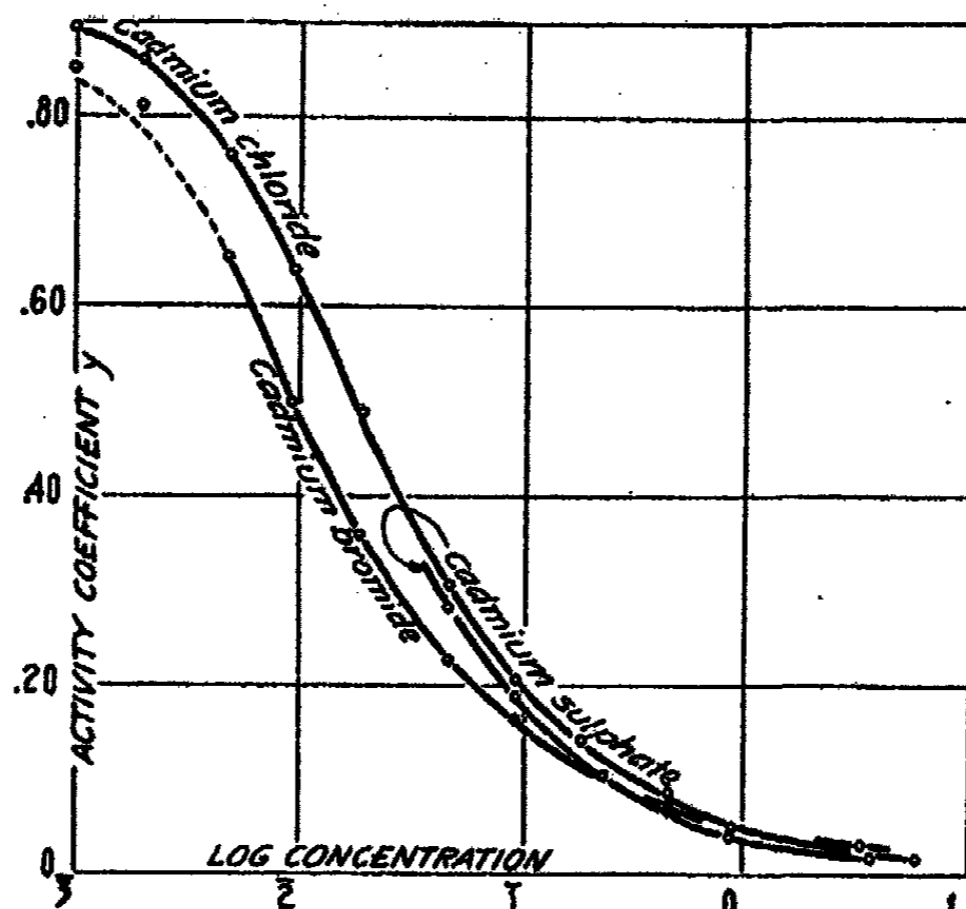
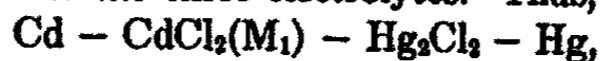


FIG. 2

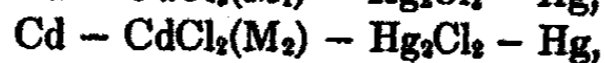
The curves of Fig. 2 are plotted from the data of Tables IV-VI, and represent the activity coefficients as a function of the logarithm of the concentration. Owing to the ease with which mercurous sulphate forms a basic salt in the more dilute solutions of cadmium sulphate, no attempt has been made to calculate the activity coefficients for cadmium sulphate at concentrations below 0.05 molal. It was this unsatisfactory behavior of mercurous sulphate in dilute solutions which led Horsch² and others to abandon its use as a depolarizer.

Free Energy of Dilution

From the data recorded in the above tables it is possible to compute the free energy of dilution accompanying ten-fold changes in concentration in the solutions of each of the three electrolytes. Thus, if we have two cells



and



the free energy of dilution, ΔF , accompanying the change from concentration M_1 to concentration M_2 is given by the formula

$$\Delta F = \frac{2 \times \Delta E \times 96500}{4.182},$$

¹ Noyes and Falk: J. Am. Chem. Soc., 34, 475 (1912).

² Horsch: loc. cit.



ACTIVITY OF SOME SALTS OF CADMIUM

where ΔE is the difference in electromotive force of the two cells, 4.182 is the electrical equivalent of heat and 96500 coulombs is the faraday equivalent. The data of the subjoined tables have been computed in this manner.

TABLE VII

Free Energy of Dilution of Cadmium Chloride

| Conc. (M ₁) | Conc. (M ₂) | ΔE | ΔF |
|-------------------------|-------------------------|------------|------------|
| 1.0 | 0.1 | 0.0380 | 1754 cal. |
| 0.5 | 0.05 | 0.0393 | 1814 |
| 0.1 | 0.01 | 0.0467 | 2206 |
| 0.05 | 0.005 | 0.0542 | 2502 |
| 0.01 | 0.001 | 0.0760 | 3503 |
| 0.005 | 0.0005 | 0.0815 | 3761 |

TABLE VIII

Free Energy of Dilution of Cadmium Bromide

| Conc. (M ₁) | Conc. (M ₂) | ΔE | ΔF |
|-------------------------|-------------------------|------------|------------|
| 1.0 | 0.01 | 0.0472 | 2178 cal. |
| 0.5 | 0.05 | 0.0472 | 2178 |
| 0.1 | 0.01 | 0.0470 | 2169 |
| 0.05 | 0.005 | 0.0467 | 2155 |
| 0.01 | 0.001 | 0.0685 | 3161 |

TABLE IX

Free Energy of Dilution of Cadmium Sulphate

| Conc. (M ₁) | Conc. (M ₂) | ΔE | ΔF |
|-------------------------|-------------------------|------------|------------|
| 1.0 | 0.1 | 0.0250 | 1154 cal. |
| 0.5 | 0.05 | 0.0245 | 1131 |
| 0.1 | 0.01 | 0.0247 | 1140 |
| 0.05 | 0.005 | 0.0243 | 1122 |

Thermochemical Data

As is well known, the thermal change accompanying a chemical reaction can be readily calculated from the measured values, at several different temperatures, of the electromotive force of a cell in which the particular reaction takes place. Thus, on substituting in the Gibbs-Helmholtz equation,

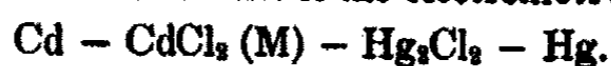
$$Q = 0.2389 NF \left(E + T \frac{dE}{dT} \right),$$

the observed value of E , at temperature T , and the value of dE/dT , derived from the observed variation of E with T , we can calculate the value of Q , the heat of the cell reaction at temperature, T .

In this manner, Lipscomb and Hulett¹ computed the heat of the reaction,

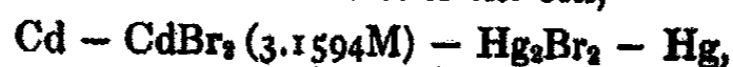


to be 30,060 cal. from measurements of the electromotive force of the cell,



Since the heat of the reaction is numerically equal to the difference between the heats of formation of the two salts, CdCl_2 and Hg_2Cl_2 , it follows that if the heat of formation of the latter is known, the heat of formation of CdCl_2 can be calculated. After making due allowance for the heat of hydration of the cadmium salt, the heat of formation of CdCl_2 , as calculated from Lipscomb and Hulett's data, is found to be 93,710 cal. The value for the heat of formation of this salt according to Thomsen² is 93,240 cal.

In like manner we have computed the heat of formation of CdBr_2 from measurements of the electromotive force of the cell,



at 15.5°, 18.7° and 25°. The value of E_{25° was found to be 0.60506 volt and $dE/dT = 0.000163$. Hence, on substituting in the Gibbs-Helmholtz equation, we have

$$\begin{aligned} Q &= 2 \times 96500 \times 0.2389 (0.60506 - 298 \times 0.000163), \\ &= 25,659 \text{ cal.} \end{aligned}$$

The values of the heat of formation of Hg_2Br_2 recorded in Landolt and Boernstein's tables are as follows: 49,000 cal. (Nernst) and 49,200 cal. (Varet). Taking 49,100 cal. as the probable value of the heat of formation of Hg_2Br_2 , it follows that the heat of formation of CdBr_2 is 74,759 cal. This is in close agreement with the value found in a similar manner by Oblata³ viz., 74,700 cal.

No attempt was made to determine the temperature coefficient of cadmium sulphate cells since this has been measured repeatedly in connection with the numerous studies which have been made of both saturated and unsaturated Weston cells.

Discussion of Results

The measured values of electromotive force recorded in Tables I-III when plotted against the logarithm of the corresponding concentration, as in Fig. 1, are found to lie on smooth curves and to show relatively little deviation, except in the most dilute solutions. At high dilutions, however, not only does the increasing solubility of the depolarizer tend to lower the electromotive force of the cells, but errors whose origin is more or less obscure become accentuated as the concentration is diminished. In the more concentrated solutions, it is believed that the values of the electromotive force are accurate to within a few tenths of a millivolt, while in the most dilute solutions the estimated error rarely exceeds 0.001 volt. The errors in the values of the activity coefficients derived from these measurements are like-

¹ Lipscomb and Hulett: loc. cit.

² Thomsen: "Thermochemische Untersuchungen," 3, 201 (1883).

³ Oblata: Proc. Phys. Math. Soc. Japan, (3) 3, 64 (1921).

wise greatest in the most dilute solutions, but in no case is it believed that the error exceeds one percent. The values of γ given in the fourth and fifth columns of Table IV show satisfactory agreement in the more concentrated solutions with the experimental data of Horsch.

The approximate values of γ for solutions of cadmium bromide, estimated from their conductance ratios, and the corresponding conductance ratios and activity coefficients of cadmium chloride show remarkable agreement.

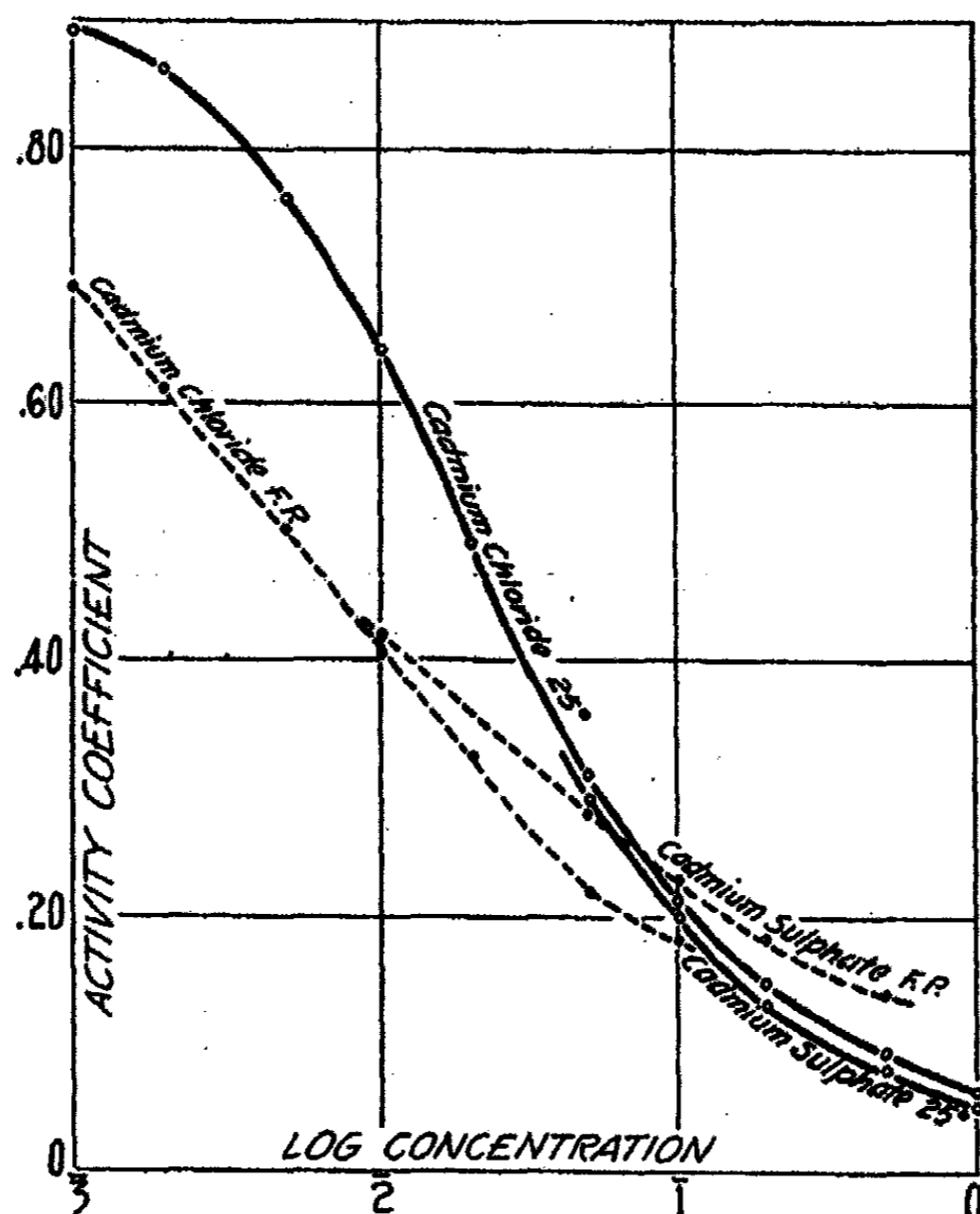


FIG. 3

Similar estimated values of γ given in the sixth column of Table VI show less satisfactory agreement. This is not surprising, however, since the manner of dissociation of cadmium sulphate is not strictly comparable with that of the chloride. The values of the activity coefficients of solutions of the cadmium halides apparently differ more widely from each other than do the activity coefficients of solutions of the alkali halides.

Lewis and Randall¹ have derived an equation by means of which the activity coefficient of a solution can be calculated from its freezing point provided the latter is known with accuracy. If we neglect the heat of dilution of the electrolyte, the equation takes the form,

¹ Lewis and Randall: "Thermodynamics," 347 (1923); Lewis and Linhart: J. Am. Chem. Soc., 41, 1952 (1919).

$$\log \gamma = \int_0^m -j \, d \log m - \frac{j}{2.303} + \frac{0.00025}{\nu} \int_0^m \frac{\theta}{m} \, d \theta,$$

where

$$j = 1 - \frac{\theta}{\nu \lambda m},$$

θ being the freezing point depression of the solvent, ν the number of ions into which the electrolyte dissociates, $\lambda = 1.858$ and m the molality of the solution. On applying this equation to the best available freezing point data, Lewis and Randall¹ computed the activity coefficients of solutions of cadmium sulphate at different concentrations. The data thus obtained, together with the values of γ given in Table VI, are represented graphically in Fig. 3. The results based upon freezing point data are represented by crosses and dotted curves, whereas the values derived from electromotive force measurements are represented by circles and full-line curves. It will be noted that the two curves are not coincident, and that the activity coefficients at 25°C. change more rapidly with concentration than do the activity coefficients of the same solution in the neighborhood of 0°C. Owing to the well-known tendency of cadmium salts to form complexes in solution this behavior is not altogether surprising.

A computation similar to that of Lewis and Randall has been made for solutions of cadmium chloride. Owing to the lack of thoroughly reliable freezing point data for this salt no claim is made for the accuracy of the results, but inspection of Fig. 3, in which the computed values of γ are plotted, reveals a marked similarity between the curves representing the values of γ for solutions of cadmium chloride, as derived from freezing point and electromotive force data respectively, and the corresponding curves for solutions of cadmium sulphate.

Summary of Results

- (1) The following cells have been studied:
 - (1) $\text{Cd} - \text{CdCl}_2(M) - \text{Hg}_2\text{Cl}_2 - \text{Hg}$,
 - (2) $\text{Cd} - \text{CdBr}_2(M) - \text{Hg}_2\text{Br}_2 - \text{Hg}$,
 - (3) $\text{Cd} - \text{CdSO}_4(M) - \text{Hg}_2\text{SO}_4 - \text{Hg}$.
- (2) From the values of the electromotive forces, at 25°C., the activity coefficients of the chloride, bromide and sulphate of cadmium at concentrations ranging from 0.001M to saturation have been calculated.
- (3) The values of the activity coefficients thus obtained have been compared with the corresponding values of the activity coefficients of the same salts as estimated from both conductivity and freezing point data.
- (4) The free energy of dilution attending the transfer of one mol of each of the foregoing cadmium salts from concentration M_1 to concentration M_2 has been computed.
- (5) The heats of formation of the chloride and bromide of cadmium have been calculated by means of the Gibbs-Helmholtz equation from the heats of the respective cell reactions.

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¹ Lewis and Randall: "Thermodynamics" 344, 362 (1923).

SOME PHYSICO-CHEMICAL PROPERTIES OF STANNOUS OXIDE

BY COLIN G. FINK¹ AND C. L. MANTELL²

This work was originally done in connection with a physico-chemical study of the reduction of tin oxides by reducing gases.³ Very little accurate data in reference to stannous oxide exists in the literature. Stannous oxide is a blue-black, iridescent, crystalline substance. It is reduced by some reducing agents. On the other hand, even mild oxidizing agents readily oxidize it to stannic oxide or metastannic acid. It is easily soluble in non-oxidizing mineral acids and in a number of organic acids to form the corresponding stannous salt. Stannous oxide is ordinarily considered as a reducing agent.

Preparation of Pure Stannous Oxide

Various experimenters have failed in attempting to get pure stannous oxide, using stannous chloride as a source, treating with soda, forming the hydroxide, heating the same, filtering and washing. Sufficient oxidation or hydration took place during these procedures so that a heavy precipitate of stannic oxide was formed.

Ditte⁴ gives the following rapid method which he claims is perfectly satisfactory for the preparation of pure stannous oxide. Stannous chloride is dissolved in water and treated while hot with the smallest amount of concentrated hydrochloric acid necessary to clear the solution. The stannous hydroxide is then precipitated by the addition of a soda solution (e. g. a carbonate) which is added in small amounts until the mixture is just alkaline to phenolphthalein but not to litmus, which is too alkaline. The milk-white solution is then kept at 110° C. for several hours. After two to three hours the white material changes to a blue-black substance, stannous oxide, with its characteristic metallic sheen. The material is then washed by decantation, dried, and made ready for use.

Fraenkel and Snipischsky⁵ repeated Ditte's method successfully. Numerous methods are proposed in the literature for SnO preparation but practically all of them, except Ditte's, produce contaminated products.

Following the method of Ditte, stannous oxide was prepared from pure, c.p. stannous chloride crystals. The strict adherence to his directions as to control of alkalinity is the most important factor in the production of pure SnO. Solutions too highly alkaline (greater than pH 7) cannot be made to yield stannous oxide even after several hours boiling. Within the range of pH 5

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² Consulting Chemical Engineer, Pratt Institute, Brooklyn.

³ Fink and Mantell: *Trans. Am. Electrochem. Soc.*, 51.

⁴ *Pogg. Ann.*, 27, 145 (1882).

⁵ *Z. anorg. Chem.*, 125, 235 (1922).

to about pH 6.5, stannous oxide can be readily produced. The product, after filtration, careful washing with distilled water to free the precipitates from chlorides, and careful drying at 110° C. is blue-black, lustrous, somewhat iridescent and decidedly crystalline. Our material corresponded exactly to SnO shown by chemical analysis for Sn by iodine titration.

SnO boiled in distilled water for half an hour did not produce any stannous hydroxide or metastannic acid as could be determined by visual examination. It did not change in color, appearance, or crystalline form, in any manner observable under the microscope.

It would, therefore, seem that the reaction:



is not readily reversible. The thermal data



show it to be endothermic.

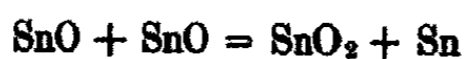
The Thermal Decomposition of Stannous Oxide

The physico-chemical properties of stannous oxide are important as they are the key of the explanation of the manner in which stannic oxide was reduced by a reducing gas.¹ The reduction of stannic oxide may be assumed to take place in either of two ways. The stannic oxide may either be reduced directly to tin metal or it may be first reduced to stannous oxide (SnO) which may be further reduced to tin metal.

The stannous oxide used was of the c.p. analyzed grade furnished by J. T. Baker Chemical Company. Chemical analysis for Sn by iodine titration showed it to be very pure as it corresponded almost exactly to the theoretical Sn percentage on a dry basis for SnO.

The literature records observations that stannous oxide is unstable above certain temperatures and therefore does not exist above this point. It is obvious that above the thermal decomposition point of stannous oxide, the reduction of stannic oxide results in the direct production of tin metal; below this point, stannous oxide may be produced.

It was desired to determine the thermal decomposition point of stannous oxide. It is readily understood that no easy chemical method exists for the separation of tin metal and stannous oxide because of their solubilities in the same reagents. It was thought that the qualitative detection of decomposition could be made by the observation of the formation of white stannic oxide. The reaction is assumed to be:



There is the objection that it is not possible, except with the most exacting care of all details, to maintain an inert gas atmosphere with a complete absence of oxygen or moisture. Both oxygen and moisture react with black stannous oxide to form the white stannic oxide. If, however, the stannic

¹ Fink and Mantell: loc. cit.

oxide formation is disregarded and only the formation of metallic tin is used as a criterion of thermal decomposition, we have a reliable method for detection of the phenomenon.

Microscopic examination by us of stannous oxide shows it to be crystalline, of the regular system, brownish black to jet black, somewhat iridescent and sparkling. The crystalline structure of finely divided or gaseous reduced tin is not observable under the ordinary microscope. It is grayish black in color. Due to its fluidity above the melting point tin forms metallic-appearing globules. The change from crystalline stannous oxide to metallic tin is easily recognized microscopically.

The apparatus set up is shown in the attached sketch. Heating of stannous oxide was done in RR alundum combustion boats in a silica tube, in an electric furnace whose current and consequent temperature was controlled by an outside resistance in series with the furnace. Temperatures were taken with a chromel-alumel (#22 gauge wire) thermocouple and a sensitive calibrated Hoskins high-resistance millivoltmeter type indicator. Heating of the SnO was done in an atmosphere of nitrogen, purified of oxygen through passage over copper wire gauze heated to 250°-300°C. in a silica tube in an electric furnace, and freed of moisture by passage through soda lime and phosphorus pentoxide. The entire system was closed and under a slight nitrogen pressure. Excess nitrogen escaped through a mercury seal at the end of the apparatus train. Between runs any copper of the gauze which had been oxidized to copper oxide was reduced by hydrogen in preparation for the next run. Any residual hydrogen was washed out by nitrogen before the run was started. The experimental results are given in Table I. Each run has been duplicated or triplicated and checked in this way.

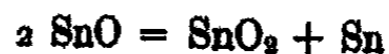
TABLE I
Stannous Oxide Decomposition

| Temperature range | Time | Observation |
|-------------------|------------|--------------------------|
| 610°-620° C. | 30 minutes | Metallic tin produced |
| 530°-540° C. | 30 " | Metallic tin produced |
| 490°-500° C. | 35 " | Metallic tin produced |
| 440°-450° C. | 60 " | Metallic tin produced |
| 420°-430° C. | 35 " | Metallic tin produced |
| 400°-420° C. | 35 " | Metallic tin produced |
| 395°-400° C. | 30 " | Metallic tin produced |
| 390°-395° C. | 40 " | Metallic tin produced |
| 375°-385° C. | 60 " | No metallic tin produced |
| 340°-360° C. | 70 " | No metallic tin produced |

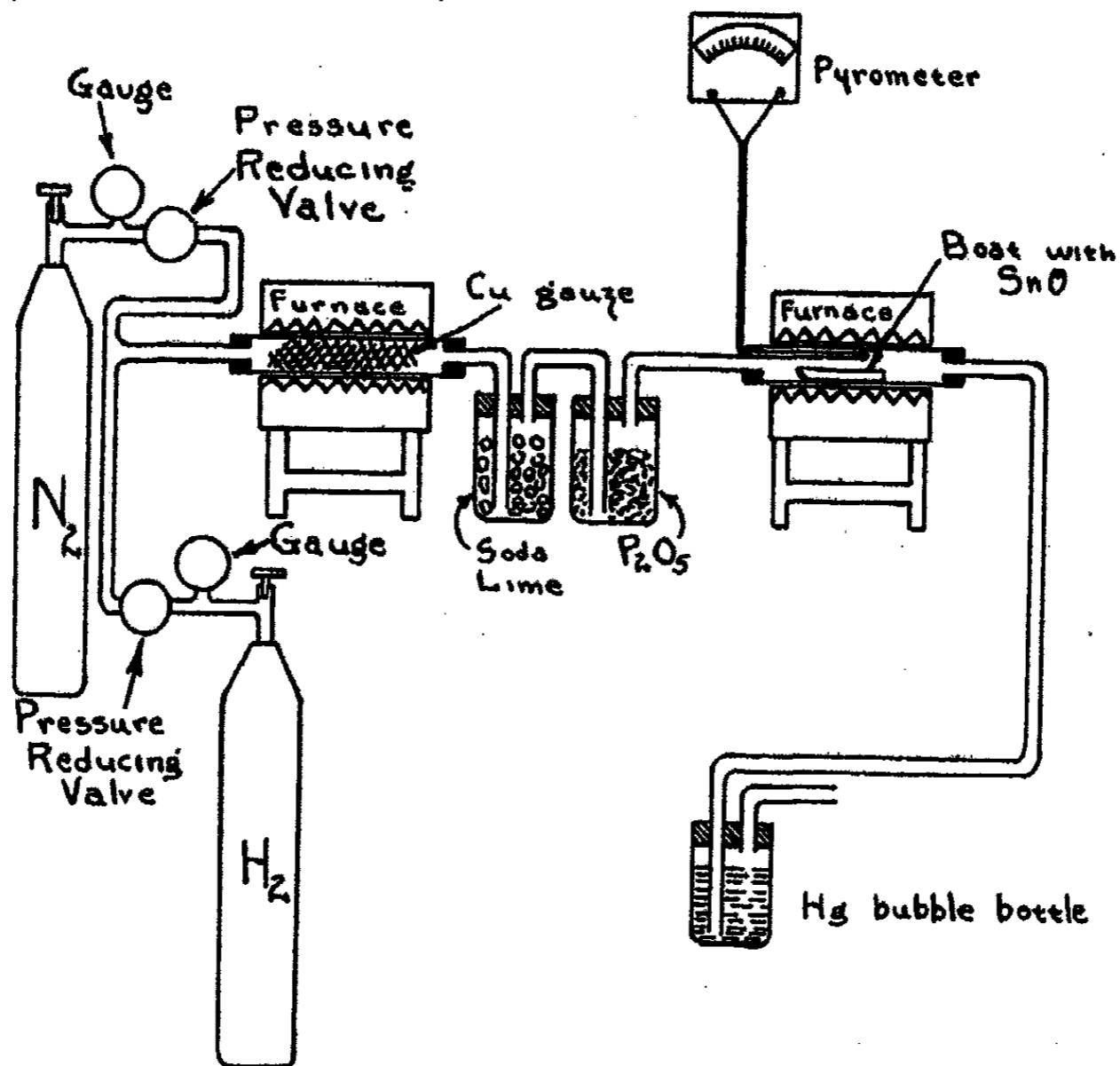
Stannous oxide is therefor thermally decomposable above 385° c. and is thermally stable below this point.

Temperatures taken with a chromel-alumel couple and high-resistance millivoltmeter. Instrument, leads, and couples were calibrated together.

It is interesting to note that Ditte¹ found that at high temperatures SnO is unstable and decomposed according to the reaction:



Fraenkel and Snipischky² confirmed this and found that stannous oxide was unstable above 500° C.



Set-up for Determination of SnO Decomposition

FIG. 1

Our work shows that the above observations were correct but that the reaction takes place at much lower temperatures. It has been shown that stannous oxide is thermally decomposable above 385°-390° C. and is thermally stable below this point.

The reaction $\text{SnO}_2 + \text{H}_2$ can therefore not be assumed to be a two-step process of reduction above this temperature. Above 385° C. we then have the reaction:

¹ Pogg. Ann., 27, 145 (1882).

² Z. anorg. Chem., 125, 235 (1922).

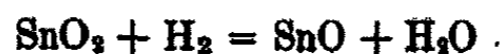


perhaps interpreted as the summation reaction of:



There is considerable doubt whether the reaction proceeds as described with the reduction of SnO_2 to SnO with very rapid decomposition of the SnO to form Sn and SnO_2 .

Below the thermal decomposition point of SnO , the reduction of stannic oxide by hydrogen takes place in two stages: x



each of which can be observed. The temperature at which reduction takes place can be regulated so as to allow the formation of SnO . We have proved this point repeatedly by experiment.

As additional data for the interpretation of the means of reduction of stannic oxide, the oxidation of stannous oxide was investigated.

The Oxidation of Stannous Oxide

Compressed air was used as an oxidizing material. The air was reduced in pressure to such a value that it passed through the apparatus train at the rate of about five liters per hour. The air was washed by bubbling through two water wash-bottles in series. It was saturated with moisture at the same time. The air was cleaned of dust particles, dirt, etc. by passage through two wash bottles in series, one filled with glass wool and the other with absorbent cotton. It then entered the silica furnace tube, which was heated by an electrical resistance furnace. The stannous oxide was held in white RR alundum combustion boats. Temperatures were taken at the center of the furnace (which was also the center of the combustion boat when it was in place in the furnace) by a calibrated chromel-alumel thermocouple and a high resistance indicator and leads.

The furnace was first brought up to the desired temperature, then opened, the boat of stannous oxide put in place and the furnace closed. The boat came to temperature very rapidly and the surface of the charge almost immediately. The boat and charge were then removed from the furnace, allowed to cool in a desiccator and then examined.

The criterion of oxidation was the formation of stannic oxide as determined by visual and microscopic examination. The color change when judged by comparison with a boat of unheated stannous oxide was readily observable, as stannic oxide is white and stannous oxide is black. Secondary confirmation was obtained by the insolubility of stannic oxide in dilute hydrochloric acid, in which the stannous oxide is completely soluble.

The data and results are given in Table II. Above 235° C. stannous oxide is instantaneously oxidizable in moist air. It burns like tinder and is almost pyrophoric in its action.

Three runs were made, at 225° C., 230° C. and 235° C. over measured time intervals to determine whether the stannous oxide was affected over an appreciable time interval. These results are also tabulated and show that at 225° C. stannous oxide is not affected by moist air after a ten minute period. It is, therefore, concluded that from 225° C. to 235° C. stannous oxide is oxidized at a slower rate than above 235° C. Below 225° C. it is not readily oxidized by moist air.

TABLE II
SnO Oxidation

| Instantaneous Temperature | | Observation |
|---------------------------|--|----------------------------------------------------------|
| 410° C. | | White stannic oxide produced, oxidation |
| 360° C. | | " " " " oxidation |
| 325° C. | | " " " " oxidation |
| 300° C. | | " " " " oxidation |
| 275° C. | | " " " " oxidation |
| 250° C. | | " " " " oxidation |
| 240° C. | | " " " " oxidation |
| 235° C. | | No white stannic oxide produced, therefore no oxidation. |

| Temperature | Time | Observation |
|-------------|-----------|-----------------------------------------------------------------------|
| 230° C. | 5 minutes | No white stannic oxide produced, therefore no oxidation. |
| 225° C. | 10 " | No white stannic oxide produced, therefore no oxidation |
| 235° C. | 10 " | No appreciable oxidation, very small amount of stannic oxide produced |

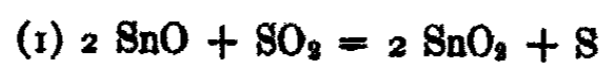
Air, saturated with moisture, was blown through the tube in which the stannous oxide was heated. Material after experiment examined macroscopically and microscopically. Temperatures taken with a Chromel-Alumel couple and high resistance voltmeter. Instrument, leads and couple were calibrated together against a standard platinum-platinum rhodium couple and precision potentiometer.

Duplicate determinations were made at the same temperatures, substituting dried air for the moist air. The air supply was the same as in the experiments but the air was cleaned and dried by bubbling through a wash-bottle of concentrated sulphuric acid, a tower packed with glass wool and absorbent cotton in alternate layers, and two soda lime towers in series. The results were quite analogous to those of moist air. Dry air effected oxidation at temperatures as low as 220° C. but not as low as 210° C. after ten minutes exposure to the warm air.

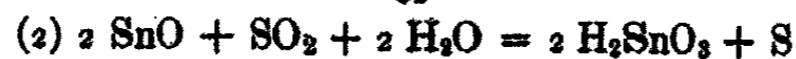
It is concluded that above 240° C. stannous oxide is readily changed to stannic oxide by both dry and moist air. At this and higher temperatures stannous oxide has pyrophoric tendencies, which increase with rise of temperature.

Oxidation of Stannous Oxide by Sulphur Dioxide in Solution

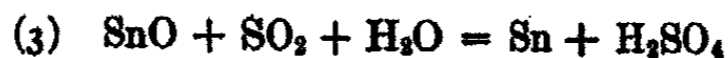
In the course of some work on the leaching of tin ores, sulphur dioxide in saturated solution was used as an aid in experimental leaching as an addition to other materials being used. Paralleling these experiments stannous oxide was leached with the same solutions. It was noticed that often the black stannous oxide was changed to a white or cream colored precipitate having the physical appearance and chemical characteristics of metastannic acid or stannic oxide. This would be in accordance with the reaction:



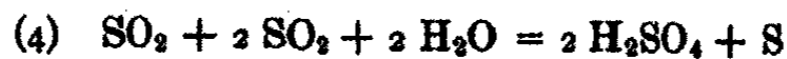
or



In other cases it was noticed that tin metal in finely divided form resulted from the action of SO_2 on stannous oxide very likely according to the reaction:



It is barely possible that the following reaction might occur and produce sulphur, but no metastannic acid could be produced by this reaction:



This reaction is just barely possible thermodynamically and was studied in considerable detail by P. D. V. Manning at the California Institute of Technology, but the results of the study have not been published.

To uphold the contention that (1) in respect to stannous oxide in acid solutions wherein the pH is less than 7, sulphur dioxide is an *oxidizing* agent toward stannous oxide; and that (2) in alkaline solutions wherein the pH is greater than 7 sulphur dioxide is a *reducing* agent toward stannous oxide, the data supporting this contention are given in Table III. It will be noticed that the presence of sulphur dioxide is always associated with the formation of dense white or cream colored precipitates in solutions acid in reaction. This precipitate was shown to be a form of stannic acid by chemical tests. In alkaline solutions the presence of sulphur dioxide is associated with the appearance of metallic tin, either as tin crystals, or sponge tin, or as a metal mirror on the walls of the bottle. The presence of tin as such was proven chemically.

All the solutions were in contact with the stannous oxide for a period of several months. Each bottle and its contents had been agitated for 168 hours, excess stannous oxide being in each bottle, in all cases. The bottles were of the four ounce oil sample size. Agitation was caused to take place at 40 R.P.M. which speed allowed the solid particles to completely fall through the volume of the solution, as the bottles were turned over once per revolution of the shaft on which they were mounted.

TABLE III

| Solution | Solution Reaction (without SO ₂) | Observation | Conclusion |
|----------------------------------------------------------------------------------------------------|-------------------------------------------------|----------------------------------------------------------------------------------------------------|--------------|
| M/3 Na ₂ SO ₄ ·10H ₂ O Saturated SO ₂ | neutral | S ppted., also bulky gray white ppt. whose volume was about 4 times that of original SnO. | SnO oxidized |
| M/1 NaHSO ₃ Saturated SO ₂ | acid | S ppted., also bulky white flocculent ppt. | SnO oxidized |
| M/1 NH ₄ Cl Saturated SO ₂ | acid | Yellow sulphur ppted., also white or cream color amorphous ppt. | SnO oxidized |
| M/2 FeSO ₄ (NH ₄) ₂ SO ₄ Saturated SO ₂ | acid | Yellow sulphur ppted., also a white amorphous ppt. in volume 4 to 5 times that of the original SnO | SnO oxidized |
| M/2 NaCl Saturated SO ₂ | neutral | Sulphur ppted., also white precipitate of metastannic acid | SnO oxidized |
| N/1 NaHSO ₃ | acid | Cream colored ppt., of large volume | SnO oxidized |
| M/1 NaHSO ₃ 2M NaOH | alkaline | Sponge tin metal layer on top of a layer of unchanged SnO | SnO reduced |
| M/10 Na ₂ SO ₃ | alkaline | Small quantity of tin produced as mirror on the side of the bottle. | SnO reduced |

Sulphur and tin were both determined chemically in a qualitative manner. All the white or cream colored precipitates were identified as forms of stannic acid by qualitative chemical tests.

To show that the cause of the oxidation is the presence of the SO₂, observations were made in solutions in which SO₂ was not present. Similar solutions in respect to anions and cations were used. They were both alkaline and acid in reaction and were similar to those solutions in which the SO₂ had been used. The results are given in Table IV.

TABLE IV

| Solution | Solution Reaction | Observation | Conclusion |
|------------------------------------------|-------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------|
| M/10 KHSO ₄ | acid | No change in layer of undissolved SnO, which was its original brownish black. No sulphur ppt. No white or other ppt. in solution | Noreduction or oxidation of SnO |
| M/1 Mn SO ₄ 4H ₂ O | acid | as above | as above |
| M/1 NH ₄ Cl | acid | as above | as above |
| M/2 CuSO ₄ 5H ₂ O | acid | Very thin layer of white substance on top of unchanged brownish black layer of unchanged SnO. White layer not stannic acid as shown by test. S, as such, absent | as above |
| M/10 MgSO ₄ | acid | As M/10 KHSO ₄ above | as above |
| 2M NaCNS | alkaline | as above | as above |
| M/1 KCN | alkaline | as above | as above |

From the data tabulated in this report, it is believed that the conclusion is warranted that in acid solutions sulphur dioxide is an oxidizing agent toward stannous oxide but that in alkaline solutions the reverse is true and that sulphur dioxide there is a reducing agent toward stannous oxide. In acid solutions the reaction favored is of the nature:



while in alkaline solutions the favored reaction is:



The free acid being neutralized by the alkali in the solution to form a sulphate. Sulphates were found by qualitative chemical tests in those solutions originally without sulphates.

It is, therefore, concluded that sulphur dioxide would be valueless in acid solutions as an aid to the solution of tin concentrates. It can not be used in leaching solutions for treatment of tin ores.

Conclusions

Stannous oxide can be readily prepared in a state of high purity if due precautions are taken to have proper pH conditions.

Stannous oxide is thermally unstable above 385°C ., giving Sn and SnO_2 .

Stannous oxide is readily oxidized by both moist and dry air above 240°C . At higher temperatures it is pyrophoric.

Stannous oxide is oxidized by sulphur dioxide in acid solutions; and reduced by the same reagent in alkaline solutions.

The reduction of stannic oxide, reasoning from the data on stannous oxide, is a single step reaction above 385°C . and a two step reaction below that temperature.

THE CATALYTIC ACTIVITY OF METALLIZED SILICA GELS

III. The Synthesis of Water

BY L. E. SWEARINGEN AND L. H. REYERSON

Ever since Sir Humphry Davy in 1817 observed that a platinum wire heated below redness, promoted the combination of hydrogen and oxygen, the catalytic synthesis of water has been the subject of much investigation. Because of the relatively simple mechanism of water synthesis it was felt that a study of this reaction would give some idea concerning the catalytic activity of metallized silica gels in oxidation reactions. Morris and Reyerson¹ have shown that metallized silica gels exhibit marked catalytic activity in hydrogenation reactions. Furthermore x-ray studies² have shown that when the metal is deposited upon the surface of the silica gel by the method described, it exists in a very fine state of division. A very large number of active catalytic centers undoubtedly exist under these conditions and the catalysts should exhibit marked activity in oxidation reactions.

Experimental

The metallized silica gels used in this research were the same as those used in the adsorption studies previously reported.³ The gases were streamed at rates varying from 15 to 300 cc. per minute through an apparent volume of 5 cc. of catalyst. The tube carrying the catalyst was maintained in a constant temperature bath and the temperature of the bath was varied from -17° in the case of the platinized and palladized gels to 290° for the copper and silver catalysts. The gas mixtures contained from about six to nine per cent of oxygen, fifty percent hydrogen and the remainder nitrogen.

A gas mixture of approximately the desired composition was first collected in a 20 liter glass bottle. Water was used as the confining liquid. After shaking and allowing to stand for several hours, a sample of the gas mixture was analysed. The gas mixture was then ready for use. An inverted glass bottle full of water supplied the pressure necessary to force the gas mixture through the catalyst train. By regulating the flow of water from the upper to the lower bottle, the velocity of the gas through the catalyst could be varied over a wide range. On leaving the container the gas mixture passed a pressure regulator which was adjusted to just allow gas to escape through it. The gas was then metered by a flow-meter which had been previously calibrated. The gas was dried before entering the catalyst tube by passing through a calcium chloride tube. Metallized gel granules having an apparent volume of 5 cc. were placed on a deep U tube which was similar to the tube described by Morris and Reyerson. A thermometer was kept imbedded in

¹ Morris and Reyerson: *J. Phys. Chem.*, 31, 1220 (1927).

² Reyerson, Harder and Swearingen: *J. Phys. Chem.*, 30, 1623 (1926).

³ Reyerson and Swearingen: *J. Phys. Chem.*, 31, 88 (1927).

the catalyst in order to note any rise in the temperature of the catalyst above that of the bath in which the catalyst tube was immersed. On leaving the catalyst tube the gas was first bubbled through a wash-bottle containing water in order to cool the gases and then led into the gas analysis apparatus. This was a modified Orsat apparatus. It contained absorption pipettes filled with small glass tubes and a water-jacketed gas-measuring burette of 100 cc. capacity. The manifold of the Orsat apparatus was closed with two-way stop cocks in such a manner that the gases flowing from the catalyst could be passed through the manifold by-passed around it. Except during analysis the gas flowed continuously through the manifold. The burette and pipettes were separated from the manifold by glass stop cocks. In this investigation the oxygen content of the gas mixture was the only thing determined. The oxygen was absorbed in an alkaline solution (1500 gm. of KOH per liter of water) of pyrogallol containing 10 gm of pyrogallic acid per 100 gm. of solution.

The catalyst tube was kept immersed in a bath for temperature control. Above 150° solder metal was used, between 100° and 150° Wood's metal was used and below 100° water or ice and ice salt mixtures were used. The bath was well insulated and constant temperatures could be maintained to within a degree or two at the higher temperatures. The temperature was always taken at the time of sampling for analysis.

Experiments were carried out showing the effect of temperature on the combination of hydrogen and oxygen in the presence of the copper and silver gel catalysts. Since the reaction was practically complete at all temperatures in the case of the platinized and palladized gels when the rate of flow was low, a study was made of the efficiency of the catalysts at various rates of flow for several temperatures.

Results

The results of the experimental work are presented in Tables I to IV. When two columns are given under the heading temperature, the column to the left gives the temperature of the bath in which the catalyst tube is immersed while the column to the right gives the temperature as recorded by the thermometer imbedded in the catalyst. In the cases where only one column is given, the temperature recorded was that of the bath. This also indicated that the thermometer in the catalyst recorded the same temperature as that in the bath. Fig. 1 shows graphically the effect of temperature upon the efficiency of copper and silver catalysts in promoting the water synthesis. The rates of flow were low. Fig. 2 illustrates the effect of changing the rate of flow on the efficiency of the more active platinum and palladium catalysts. Three temperatures are given for each catalyst, and the temperatures are those of the bath surrounding the catalyst tube.

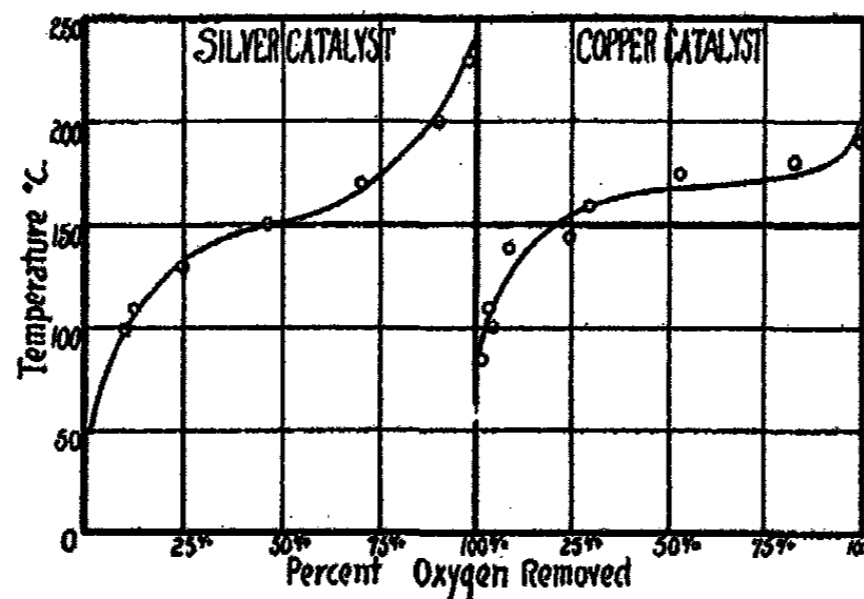


FIG. 1
Effect of Temperature on Combination of H₂ and O₂

TABLE I

Silver Catalyst

Gas Mixture: 6.50% Oxygen, 50.00% Hydrogen, 43.50% Nitrogen.

| Temperature | Rate of Flow, cc. per Minute | Percent Oxygen in Residual Gas | Percent Oxygen removed |
|-------------|------------------------------|--------------------------------|------------------------|
| 300 | 24 | 0.00 | 100.00 |
| 260 | 24 | 0.00 | 100.00 |
| 230 | 24 | 0.00 | 100.00 |
| 230 | 24 | 0.20 | 97.00 |
| 225 | 24 | 0.20 | 97.00 |
| 224 | 24 | 0.00 | 100.00 |
| 218 | 24 | 0.20 | 97.00 |
| 202 | 24 | 0.41 | 94.20 |
| 200 | 24 | 0.60 | 90.80 |
| 187 | 24 | 0.80 | 87.70 |
| 182 | 24 | 1.00 | 84.60 |
| 170 | 24 | 1.95 | 70.00 |
| 150 | 24 | 3.00 | 46.20 |
| 133 | 24 | 4.80 | 26.20 |
| 122 | 24 | 4.87 | 25.10 |
| 110 | 24 | 5.60 | 13.85 |
| 100 | 24 | 5.80 | 10.75 |

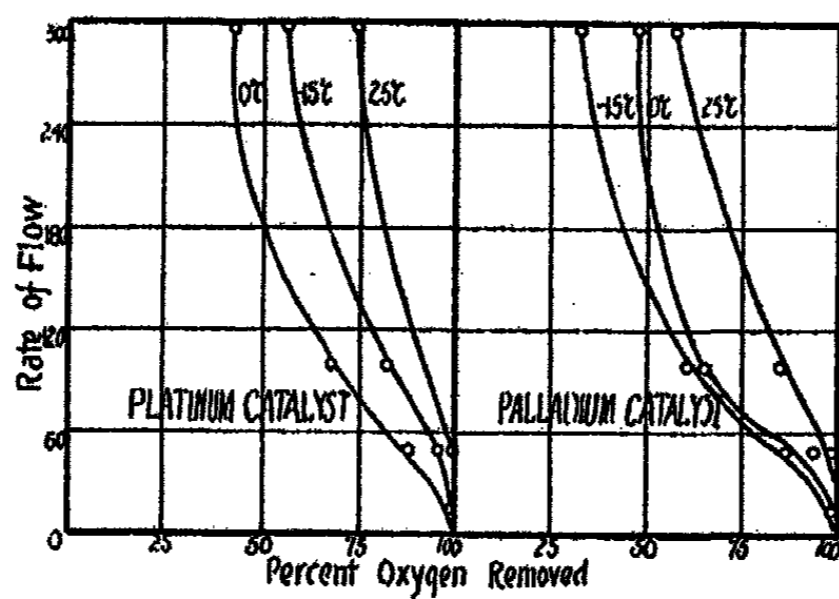


FIG. 2
Effect of Rate of Flow on the Combination of H_2 and O_2

TABLE II
Copper Catalyst

Gas Mixture: 7.00% Oxygen, 50.00% Hydrogen, 43.00 Nitrogen.

| Temperature | Rate of Flow, cc. per Minute | Percent Oxygen in Residual Gas | Percent Oxygen removed |
|-------------|---------------------------------|-----------------------------------|---------------------------|
| 195 | 38 | 0.00 | 100.00 |
| 175 | 38 | 2.93 | 58.20 |
| 174 | 38 | 3.57 | 49.00 |
| 151 | 38 | 5.42 | 22.60 |
| 143 | 38 | 5.13 | 26.75 |
| 141 | 38 | 5.44 | 22.30 |
| 124 | 38 | 6.35 | 9.30 |
| 100 | 38 | 6.44 | 8.00 |
| 220 | 38 | 0.00 | 100.00 |
| 200 | 38 | 0.00 | 100.00 |
| 197 | 28 | 0.00 | 100.00 |
| 192 | 38 | 0.00 | 100.00 |
| 185 | 38 | 1.34 | 83.40 |
| 174 | 38 | 1.49 | 81.25 |
| 166 | 38 | 5.54 | 30.80 |
| 155 | 38 | 5.70 | 28.80 |
| 140 | 38 | 6.73 | 15.90 |
| 110 | 38 | 7.34 | 7.50 |
| 90 | 38 | 7.70 | 3.75 |
| 80 | 38 | 7.67 | 4.15 |

TABLE III
Platinum Catalyst
Gas Mixture: 9.20% Oxygen, 50.00% Hydrogen, 40.80% Nitrogen.

| Temperature | Rate of Flow cc. per Minute | Percent Oxygen in Residual Gas | Percent Oxygen removed | |
|-------------|--------------------------------|-----------------------------------|---------------------------|--------|
| Bath | Catalyst | | | |
| 24 | 25 | 15 | 0.00 | 100.00 |
| 24 | 25 | 15 | 0.00 | 100.00 |
| 24 | 25 | 15 | 0.00 | 100.00 |
| 24 | 26 | 50 | 2.21 | 76.00 |
| 24 | 27 | 50 | 1.61 | 82.50 |
| 24 | 26 | 50 | 0.00 | 100.00 |
| 24 | 26 | 50 | 0.00 | 100.00 |
| 24 | 26 | 50 | 0.00 | 100.00 |
| 25 | 38 | 300 | 2.13 | 77.00 |
| 25 | 38 | 300 | 2.50 | 73.00 |
| 25 | 36 | 300 | 2.59 | 71.80 |
| 0 | 6 | 15 | 2.51 | 71.30 |
| 0 | 7 | 15 | 0.16 | 99.00 |
| 0 | 4 | 15 | 0.00 | 100.00 |
| 0 | 7 | 15 | 0.00 | 100.00 |
| 0 | 8 | 50 | 0.83 | 90.00 |
| 0 | 9 | 50 | 1.21 | 86.00 |
| 0 | 9 | 50 | 1.00 | 88.00 |
| 0 | 12 | 100 | 3.10 | 64.50 |
| 0 | 10 | 100 | 2.57 | 70.50 |
| 0 | 10 | 100 | 2.65 | 69.50 |
| 0 | 14 | 300 | 4.78 | 45.00 |
| 0 | 15 | 300 | 4.93 | 43.40 |
| 0 | 15 | 300 | 4.80 | 44.80 |
| -16 | -10 | 15 | 4.55 | 48.50 |
| -16 | -10 | 15 | 0.00 | 100.00 |
| -16 | -10 | 15 | 0.00 | 100.00 |
| -16 | -10 | 15 | 0.00 | 100.00 |
| -15 | 0 | 50 | 0.28 | 96.80 |
| -15 | -5 | 50 | 0.27 | 96.90 |
| -15 | 0 | 50 | 0.30 | 96.60 |
| -15 | 5 | 100 | 1.67 | 81.00 |
| -15 | 5 | 100 | 1.56 | 82.00 |
| -15 | 4 | 100 | 1.50 | 82.70 |
| -15 | 15 | 300 | 3.78 | 56.60 |
| -15 | 15 | 300 | 3.83 | 56.10 |
| -15 | 16 | 300 | 3.90 | 55.20 |

TABLE IV
Palladium Catalyst
Gas Mixture: 9.20% Oxygen, 50.00% Hydrogen, 40.80% Nitrogen.

| Temperature | | Rate of Flow, cc. per Minute | Percent Oxygen in Residual Gas | Percent Oxygen removed |
|-------------|----------|---------------------------------|-----------------------------------|---------------------------|
| Bath | Catalyst | | | |
| 25 | 26 | 15 | 0.00 | 100.00 |
| 25 | 26 | 15 | 0.00 | 100.00 |
| 25 | 26 | 15 | 0.00 | 100.00 |
| 25 | 26 | 50 | 0.00 | 100.00 |
| 25 | 26 | 50 | 0.00 | 100.00 |
| 25 | 28 | 50 | 9.00 | 100.00 |
| 25 | 28 | 50 | 0.00 | 100.00 |
| 25 | 33 | 100 | 1.75 | 81.00 |
| 25 | 36 | 100 | .87 | 90.50 |
| 25 | 35 | 100 | 1.20 | 87.00 |
| 25 | 40 | 300 | 3.93 | 57.30 |
| 25 | 41 | 300 | 3.88 | 57.80 |
| 25 | 41 | 300 | 3.80 | 58.80 |
| 0 | 2 | 15 | 0.00 | 100.00 |
| 0 | 2 | 15 | 0.00 | 100.00 |
| 0 | 3 | 15 | 0.00 | 100.00 |
| 0 | 10 | 50 | 0.71 | 92.40 |
| 0 | 8 | 50 | 0.42 | 95.50 |
| 0 | 9 | 50 | 0.56 | 94.00 |
| 0 | 16 | 100 | 3.19 | 65.40 |
| 0 | 17 | 100 | 3.06 | 66.80 |
| 0 | 16 | 100 | 3.00 | 67.49 |
| 0 | 21 | 300 | 4.56 | 50.40 |
| 0 | 20 | 300 | 4.92 | 46.60 |
| 0 | 21 | 300 | 4.78 | 48.10 |

Gas Mixture: 8.70% Oxygen, 50.00% Hydrogen, 42.30% Nitrogen.

| | | | | |
|-----|----|-----|------|--------|
| -17 | -4 | 15 | 0.00 | 100.00 |
| -17 | -5 | 15 | 0.00 | 100.00 |
| -16 | -5 | 15 | 0.00 | 100.00 |
| -17 | 0 | 50 | 1.08 | 87.80 |
| -16 | 0 | 50 | 0.85 | 90.50 |
| -16 | 0 | 50 | 0.82 | 90.60 |
| -15 | 0 | 100 | 3.50 | 60.00 |
| -16 | 0 | 100 | 3.30 | 62.00 |
| -15 | 1 | 100 | 3.35 | 61.70 |
| -15 | 5 | 300 | 5.67 | 34.90 |
| -15 | 4 | 300 | 5.93 | 31.95 |
| -15 | 6 | 300 | 5.80 | 33.35 |

Discussion of Results

In the case of the silverized gel, Table I and Fig. 1 show that the reaction became measurable at about 100° . The continuation of the curve indicates a reaction at still lower temperature but this was not realized in the experiments. The catalyst increases in efficiency as the temperature rises. The most rapid increase comes in the temperature interval between 140° and 180° . Above 200° practically all of the oxygen is removed at the rates of streaming studied.

The copper catalyst gives a measurable reaction at a lower temperature than the silver catalyst. The reaction is measurable at 80° . There is a rather steady increase in the amount of reaction until 165° is reached when there is a rapid rise in the efficiency of the catalyst. The catalyst becomes one hundred percent efficient below 200° for the rates of flow of the gas mixture studied. The curves for the silver and copper catalysts are much alike except that above 165° the efficiency of the copper catalyst increases more rapidly than does that of the silver catalyst. This copper catalyst compares favorably with the one prepared by Pease and Taylor.¹ In fact it probably initiates reaction at a slightly lower temperature.

The platinized and palladized gels on the other hand promote complete conversion of the oxygen and hydrogen at all of the temperatures studied provided the rate of gas flow was not too fast. Fig 2 shows the effect of increasing the rate at which the gas streamed through the catalyst upon the efficiency of the catalyst. The efficiency of the catalyst does not diminish as rapidly at the higher temperatures for given increases in gas flow as it does at lower temperatures. These catalysts heat up considerably as a result of the reaction and the temperature is undoubtedly much higher than that recorded by the thermometer immersed in the catalyst because the platinum catalyst was often observed to glow at local points. Tables III and IV show that increasing flow produces increasing differences between the temperature of the bath and that of the catalyst. The platinum catalyst shows a thirty degree rise in temperature at -15° for a streaming rate of 300 cc. per minute. This is the greatest difference observed in any of the experiments. The copper and silver catalysts show no differences in bath and catalyst temperature.

The most interesting result shown by these experiments is that the platinum catalyst is more efficient in promoting the synthesis of water at faster streaming rates than is the palladized gel. This is certainly true at 25° and at -15° . At 0° there is not much difference between the two catalysts. It would also appear that the platinized gel is more efficient at -15° than it is at 0° . This is probably due to the fact that at 0° the water formed by the reaction condenses in small droplets on the wall of the tube. These droplets tend to fall on the catalyst or run down the tube and onto the catalyst. Here the water is vaporized by the local heating of the catalyst granules and this steam tends to prevent the reacting gases from reaching the active surface.

¹ J. Am. Chem. Soc., 44, 1637 (1922).

At -15° the water freezes on the walls of the tube and does not interfere with the reaction. This no doubt accounts for the almost equal efficiency of the catalysts at 0° while at the other temperatures the platinized gel is considerably more efficient. At slow rates of streaming both catalysts are sufficiently active to use up the oxygen.

The present study does not make it possible to postulate a mechanism of reaction on the catalyst surface because the composition of the gas mixture was not varied.

Summary

1. The silver catalyst initiates the reaction below 100° and is practically one hundred per cent efficient above 200° at the rate of streaming studied.
2. The copperized gel initiates the reaction below 80° and the reaction is complete below 200° .
3. The platinized and palladized gels show marked activity in promoting the synthesis of water at all temperatures studied. The platinized gel is more efficient than the palladium catalyst as the rate of streaming of the gases is increased.

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THE CATALYTIC DECOMPOSITION OF FORMIC ACID VAPOUR

BY C. H. D. CLARK AND B. TOPLEY

The catalytic decomposition of formic acid vapour at the surfaces of metals, glasses, silica and metallic oxides can be explained on the view of contact catalysis, according to which the reaction takes place in an adsorbed layer one molecule thick, partially covering the catalyst surface.

The independence of the two alternative modes of decomposition on glass, viz., (1) $\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2$, and (2) $\text{HCOOH} \rightarrow \text{H}_2\text{O} + \text{CO}$, when considered in connection with the large temperature coefficients of these two reactions, makes it very probable that the interpretation in terms of the 'adsorption' mechanism is correct in this instance.¹

The simplest assumption to explain the fact of catalysis by surfaces is that the energy necessary for activation of the reactant molecules is lowered by association with the catalytic surface, but this leads one to expect a rough parallelism between temperature coefficient of reaction rate and specific catalytic activity (i.e., the catalytic activity per unit area of superficial surface). Such a parallelism might, of course, be completely masked by a wide variation in the number of molecules adsorbed per unit area; but *a priori* it would seem reasonable to expect that when the heat of adsorption is large, a considerable alteration of the activation energy would be produced, because of the 'molecular field' in which the adsorbed molecule finds itself, and, simultaneously, a *relatively* large fraction of the surface would be covered by the adsorbed layer. Further, the *positive* correction to be applied to the empirical 'energy of activation' in kinetically unimolecular reactions, on account of decreasing adsorption with rise in temperature, is equal to the heat of adsorption. If we write

$$k\sigma \cdot e^{-A/RT} \cdot e^{+\lambda/RT}, \text{ where}$$

k = rate of reaction per unit area of catalytic surface, under standard conditions of concentration of reactant vapour and volume of reaction bulb;

A = empirical energy of activation obtained from the temperature coefficient of reaction rate;

λ = heat of adsorption per gram-molecule;

R = gas constant;

σ = fraction of surface covered by a unimolecular adsorbed layer, at temperature T ;

then we might expect, in passing from one catalyst to another, that the larger values of σ would be associated with larger values of λ and smaller values of A , so that *qualitatively* there should be a correlation between $e^{-A/RT}$ and k .

Actually, there appears to be no correlation between these two experimental quantities.

¹ Hinshelwood and Topley: *J. Chem. Soc.*, 123, 1022 (1923).

Because of this, measurements of catalytic efficiency have been made for a number of metals, which have not been previously studied with the object of ascertaining whether their specific catalytic activities for one and the same reaction ($\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2$) can be related to any one property of the catalysts; for instance, on one view, it seemed possible that catalytic efficiency might be connected with the number of 'free' electrons in the metals, as measured by the excess of their specific heats over the value $3R$. In the event, however, the results were not very helpful from this point of view, because in some cases the actual effects of the metals concerned seemed to be masked by an oxide film; but it has nevertheless seemed worth while to record the experimental results which have been so far obtained.

The experimental method employed was similar to that used by Hinshelwood. The catalyst, together with a weighed amount of formic acid, contained in a narrow capillary with a very fine tip, was introduced into a bulb of known volume, which was cooled in ice, evacuated to below 0.1 mm. with a Hyvac pump, and sealed off. Vapour baths of anisol, aniline, nitrobenzene and quinoline were used to maintain suitable constant temperatures during the decomposition. The unimolecular velocity constant, reduced to 1 sq. cm. of catalyst surface in a 20 c.c. reaction bulb, is taken as a measure of the specific catalytic activity. This constant will be denoted by k .

Some experiments with osmium and tungsten were also carried out in a manometric apparatus exactly like the one already described.¹ Analyses of the gaseous products of decomposition were carried out in a Haldane apparatus.

Catalysis by Osmium

The use of osmium as a catalyst was suggested by the observation of E. Müller and K. Sponzel² that, in respect of decomposition of aqueous solutions of formic acid, the activity of metallic rhodium decreases as the purity of the metal increases, and appears to be connected with traces of osmium in the rhodium.

Metallic osmium was obtainable only in the form of a powder. A rough estimate of the effective surface of this powder was made by determining the size of the grains. The particles were 'graded' by sifting through fine copper gauze, and the number of particles determined in two ways:—

(1) By counting under a microscope the number of particles in a weighed amount of the powder; this gave 3.71×10^6 particles per gram.

(2) By the application of Stokes' Law, which gave 1×10^6 particles per gram.

From the mean of these results, the surface area of 1 gram of the powder is calculated to be 80.1 sq. cm. This represents the order of magnitude of the superficial area of the osmium catalyst.

The experiments with osmium were done with 90% formic acid. For decomposition at temperatures in the neighbourhood of 200°C, analysis of the

¹ Hinshelwood and Topley: *J. Chem. Soc.*, 123, 1022 (1923).

² *Z. Elektrochemie*, 28, 307 (1922).

reaction products showed that only hydrogen and carbon dioxide were produced. The reaction follows the unimolecular law, as the results in Table I of a typical experiment in the manometric apparatus show.

TABLE I

| Time <i>t</i> (minutes) | Pressure <i>p</i> (mm. of Hg) | $k = 1/t \log_e p^\infty / (p^\infty - p)$. |
|----------------------------|----------------------------------|----------------------------------------------|
| 20 | 116 | 0.00655 |
| 40 | 197 | 0.00645 |
| 60 | 267 | 0.00679 |
| 80 | 314 | 0.00671 |
| 100 | 349 | 0.00685 |
| End Point | 440 | |

The absolute value of the velocity constant was determined at 153.9°C, in a series of five sealed bulb experiments, the results being $k = 0.0131, 0.0078, 0.0146, 0.00767$ and 0.00903 . The average value of the unimolecular constant $k_{CO_2} = 0.0104$.

The temperature coefficient was found by using the device of allowing the reaction to take place partly at one temperature, and then to proceed to completion at a higher temperature, in the manometric apparatus. The results of experiment are given in Table II.

TABLE II

| Temperatures (°C) | k_{CO_2} | A_{CO_2} (cal.) |
|-------------------|-------------------|-------------------|
| 154.6 185.0 | 0.00477 0.0209 | 18,900 |
| 154.25 185.0 | 0.00241 0.0111 | 19,300 |
| 154.9 185.1 | 0.00319 0.0133 | 18,400 |

The value of *A* may be taken as 19,000 calories per gram, to the nearest 500 calories. Using this, the absolute magnitude of the unimolecular constant per unit area for a 20 c.c. bulb, is calculated to be 9.2×10^{-2} at 200°C.

Catalysis by Nickel

The nickel catalyst was used in the form of pure nickel foil. At the temperatures of the experiment (183° and 210°) the formic acid vapour (99.6%) reacts with the metal, hydrogen being formed; after the reaction, the bulb contained drops of a greenish liquid,—presumably a solution of nickel formate. At the same time, carbon dioxide is formed in the reaction bulb, probably as a result of direct catalytic decomposition at the metallic surface, and not by the decomposition of nickel formate, since there was no sign of a deposit of metal on the smooth surfaces of the foil.

In a typical experiment at 210°, the gas in the reaction bulb had the composition:

$$\begin{aligned} \text{H} &= 64.3\% \\ \text{CO}_2 &= 33.7\% \\ \text{CO} &= 2.0\% \end{aligned}$$

The 2.0% of carbon monoxide corresponded to the activity of the walls of the reaction bulb, which was of soda glass.

Similar results were obtained in other experiments, though the ratio of carbon dioxide to hydrogen is somewhat variable, and increases at the lower temperature.

Under the conditions of these bulb experiments, there is no formation of methane by reduction of carbon dioxide by hydrogen, as observed by Sabatier with a finely divided nickel catalyst. Westcott and Engelder,¹ also obtained no methane when decomposing formic acid vapour by passing it over a nickel catalyst between 200° and 500°.

On the assumption that the carbon dioxide is formed by the usual unimolecular reaction, independently of the simultaneous interaction of the nickel and formic acid vapour, the following rough values of k_{CO} , (calculated with natural logarithms, the unit of time being the minute) are a measure of the specific catalytic activity of nickel:—

| | k_{CO} , per 1 sq. cm. |
|-------|---------------------------------|
| 183°C | 3×10^5 |
| 210°C | 1.6×10^{-4} |

For comparison with other catalysts, the absolute magnitude of the unimolecular constant for nickel at 200°C may be taken as 1.0×10^{-4} .

Catalysis by Tungsten

The catalyst was used in the form of a thin tungsten sheet. Catalytic decomposition takes place at a rate convenient for measurement at 210°C; a manometric experiment proved that the reaction follows the unimolecular law.

The gaseous reaction product was practically pure carbon monoxide. During the reaction, the bright surface of the tungsten becomes dull and slightly blue. Since all other *metals* that have been experimented with catalyse the carbon dioxide reaction mainly, it seems likely that the explanation of the production of carbon monoxide only in this case is that a thin film of the blue oxide of tungsten is rapidly formed on the surface of the metal, which then produces the usual catalysis by oxides yielding carbon monoxide. This would account for the discolouration of the metal, and, moreover, an experiment in which the yellow oxide of tungsten was heated at 210°C in a sealed bulb with formic acid vapour resulted in the reduction of the yellow to the blue oxide.

¹ J. Phys. Chem., 30, 476 (1926).

The existence of such a thin film of oxide on tungsten is probable, according to U. R. Evans,¹ in view of the marked passivity of the metal. The reaction bulb was evacuated to rather less than 0.1 mm. of residual air, which would leave sufficient oxygen to furnish an oxide film thick enough to produce interference colours.

An interesting point is the unusual catalytic activity of this oxide film; the unimolecular constant k_{CO} per sq. cm. of superficial area of oxide layer is 2.5×10^{-3} at 210°C. This is rather higher than the constant k_{CO} for silver at the same temperature, and certainly very much greater than the specific activity of ordinary granular "blue" oxide of tungsten; possibly the association of the coherent oxide film with the underlying metal alters its properties.

Catalysis by Molybdenum and Tantalum

Both molybdenum and tantalum catalyse the decomposition, but the usual reaction $HCOOH \rightarrow H_2 + CO_2$ is not the main effect. A typical analysis of the gas obtained with molybdenum was:—

$$\begin{aligned} H &= 53.4\% \\ CO &= 6.7\% \\ CO_2 &= 39.9\% \end{aligned}$$

About one-third of the carbon monoxide and a little of the carbon dioxide in this experiment would have been due to the catalytic action of the soda glass of the reaction bulb; the excess of hydrogen is thus very marked. The interaction of formic acid and molybdenum is being further investigated.

Catalysis by Silica, Pyrex and Soda Glass

In the course of the experiments on metals, an attempt was made to find a material for the reaction vessel which would have a negligibly small catalytic activity. The specific activity of silica and of Pyrex was compared with that of soda glass. At 210°C, the products are mainly carbon monoxide and water in each case. The means of the results of many experiments are represented by the following figures:—

| | k_{CO} |
|--------------|----------------------|
| Soda Glass | 4×10^{-6} |
| Pyrex | 1.5×10^{-6} |
| Fused Silica | 1.0×10^{-6} |

Table III contains the quantitative data available as to the catalytic decomposition of formic acid vapour on the surfaces of different catalysts; the values of k are calculated in reciprocal minutes, for unit surface of the catalyst in a reaction bulb of 20 c.c., using natural logarithms.

¹ "Metals and Metallic Compounds."

TABLE III

| Catalyst | k_{CO_2} (at 200°C, per unit area). |
|------------|------------------------------------------|
| Duroglass | 2.5×10^{-7} |
| Gold | 9.2×10^{-8} |
| Silver | 1.03×10^{-8} |
| Nickel | 1×10^{-4} |
| Platinum | 4.4×10^{-4} |
| Rhodium | 2.4×10^{-3} |
| Osmium | 9.2×10^{-2} |
| (Palladium | $10^{-3} - 10^{-1}$) |

| | k_{CO} (at 210°C, per unit area). |
|-------------------------|----------------------------------------|
| Silica | 1×10^{-6} |
| Pyrex | 1.5×10^{-6} |
| Soda Glass | 4×10^{-6} |
| Tungsten (+ oxide film) | 2.5×10^{-6} |

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THE EFFECT OF TEMPERATURE ON RATE OF OSMOSIS

BY RALPH N. TRAXLER

It is a commonly recognized fact that rise in temperature causes a marked increase in the rate of osmosis and dialysis and also increases the osmotic pressure developed by a solution separated from the pure solvent by a semipermeable membrane. A review of the literature covering these subjects shows that relatively little attention has been given to the effect of temperature except in its direct effect on the osmotic pressure of a solution. H. N. Morse and his coworkers¹ and numerous others have investigated this phase of the subject quite extensively. However, nothing in a quantitative way is recorded concerning the rate of passage of material through a membrane as affected by temperature.

G. Flusin has shown by experiments on rubber membranes² and on pig's bladder³ that the direction and velocity of transfer of liquids across these membranes depend on the absorption capacity of the membrane for the liquids. Carbon disulphide which is absorbed readily by rubber passes quickly through a rubber membrane into alcohol, whereas chlorobenzene and nitrobenzene which are not readily absorbed pass through very slowly. Water which is taken up in large quantities by hog's bladder passes through rapidly and chloroform which is absorbed much less passes through proportionally slower. He decided that the velocity of osmosis did not depend on the maximum amount of absorption but upon the energy with which the membrane takes up the liquid during the first minute of contact. His experiments were carried out under controlled temperature conditions, but no attempt was made to determine the effect of different temperatures on the velocity.

The present paper records the results of experiments made to determine the effects of definite changes of temperature on the rate of establishment of equilibrium in (1) a system composed of pure pyridine separated from pure water by a thin rubber membrane and (2) a system composed of a one-half molar solution of sodium chloride in water separated from pure water by a collodion membrane.

Experiments showing the Effect of Temperature Changes on the Passage of Pyridine through a Thin Rubber Membrane into Water.

The pyridine was pure and freshly distilled before use. The water was distilled and free from dissolved gases. The rubber used for the membrane was a high grade of dental dam, very uniform in weight and quality. The thickness of the unstretched sheet was $0.3 \pm .05$ mm.

¹ Am. Chem. J., 45, 91, 237, 383, 517, (1911).

² Compt. rend., 126, 1497 (1898).

³ Compt. rend., 131, 1308 (1900).

No originality is claimed for the cell and stirring arrangement, the design of which was derived from the apparatus used by Kahlenberg¹ in his work on osmosis and dialysis. Fig. 1 gives the essential details of the apparatus.

The cell was a cylindrical nickel-plated drum, 3 centimeters in diameter and 4.2 centimeters in height. The area of the open end was 7.07 square centimeters. Around the bottom and open end of the drum was a rolled

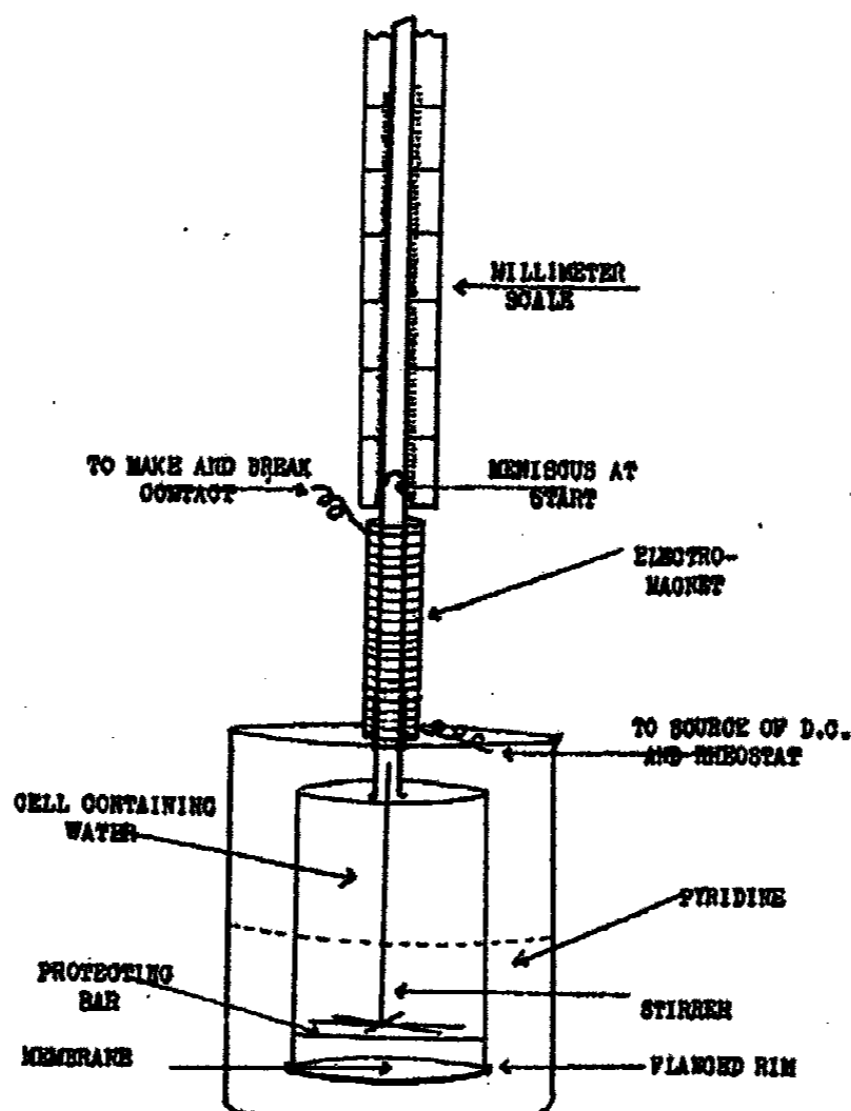


FIG. 1

flange which made it easy to fasten on the membrane. A bar was fastened across the inside of the cell about 0.5 centimeter from the bottom, the function of which was to prevent the stirrer from dropping down into direct contact with the membrane. The upper and closed end of the cell was fitted with a metallic tube 5 centimeters long and exactly the same diameter as a glass tube which was firmly fastened to it by means of rubber tubing and wire. A hollow cylinder carrying a large number of turns of fine wire formed an electro-magnet which operated the stirrer. This electro-magnet was connected to a source of direct current through a rheostat and adjustable make and break contact. The long glass tube extending up from the cell rested against a millimeter scale upon which the rise of the liquid in the cell could be conveniently read. The rubber membrane was tied over the mouth of the cell by means of strong thread, care being taken to obtain a taut surface without

¹ J. Phys. Chem., 10, 141 (1906).

stretching the rubber. After the rubber was in place a piece of new, washed muslin, weighing 0.0133 gram per square centimeter was tied over the mouth of the cell. Some such support was obviously necessary to prevent the bulging and stretching of the rubber under the weight of the column of liquid. New pieces of rubber and cloth were used for each experiment.

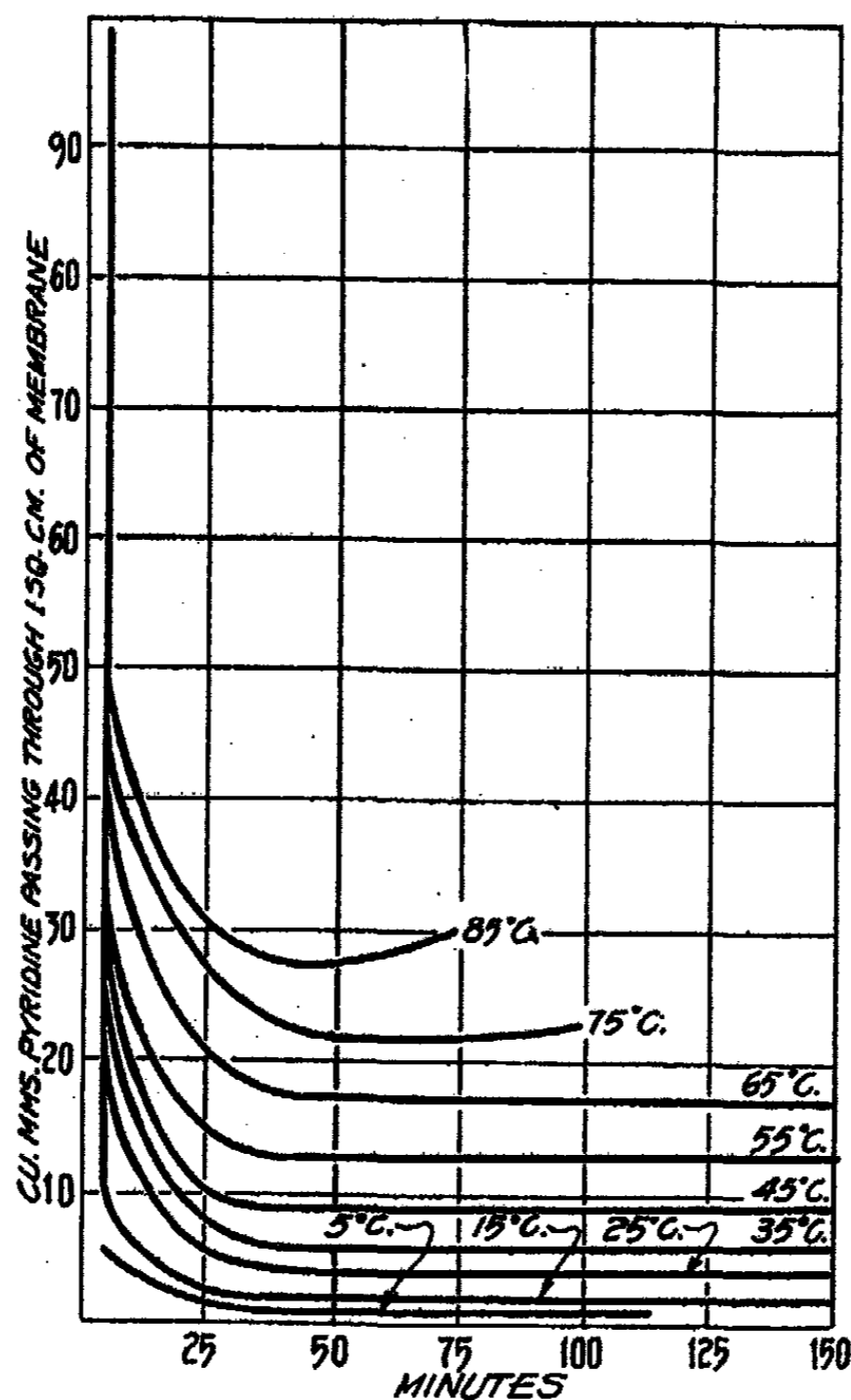


FIG. 2

The cell, filled with water and free from air bubbles and with the meniscus on the scale, was placed in a glass cup or beaker containing the pyridine. The beaker was covered by a slit cover fitting around the cell, and then placed in a thermostat capable of regulation to less than 0.5°C. The cell was always immersed to the same depth in the pyridine. The water in the cell and the pyridine in the beaker were brought to the temperature of the thermostat before lowering the cell into position.

The rise of the liquid in the glass tube was observed and recorded in centimeters. By careful calibration it was found that the tube, which was excep-

tionally uniform in bore, contained 52 cubic millimeters for every centimeter of its length. From this the scale readings were converted into volumes passing through the membrane. Dividing this value by the area of the membrane gave the volume passing through one square centimeter. These are the values used in plotting the results.

Stirring of the inner liquid took place every 18 or 20 seconds. Kahlenberg¹ has shown that stirring is absolutely necessary in quantitative measurements of osmosis and osmotic pressure. His contentions in regard to this point of technique were again shown to be correct in the experiments herein recorded. More or less rapid and uniform stirring was necessary in order to obtain uniform and concordant results in the experiments recorded below. It is only reasonable to assume that, without stirring, the pyridine passing through the rubber would form a very concentrated solution of pyridine in water which would remain in close proximity to the membrane. The pyridine would only diffuse slowly into the water in the upper part of the cell. This layer of concentrated solution would retard the flow of pyridine through the membrane. A false equilibrium would thus be set up between this layer and the pure pyridine emerging from the membrane. The purpose of the experiments is to measure the rate of attainment of equilibrium between the uniform contents of the cell and pure pyridine. Stirring the contents of the cell causes the concentration to be maintained nearly uniform throughout.

Experiments were conducted at ten degree intervals from 5°C. to 85°C. The results are given in Tables I to IX and are plotted in Fig. 2. Checking experiments were made at each temperature. To conserve space the averages are given in the tables, except at 35°C. where two runs are given to indicate the small differences usually occurring. At 65°, 75° and 85°C. the amount of error increases slightly due probably to the greater difficulties of manipulation at the higher temperatures. Toward the end of the experiments at these higher temperatures the rate of passage increased somewhat. This is shown

TABLE I
Pyridine and Water at 5°C.

| Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane | Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane |
|-----------------|-------------------------|-------------------------------------------------------------|-----------------|-------------------------|-------------------------------------------------------------|
| 0 | 3.20 | — | 50 | 6.35 | .94 |
| 5 | 3.90 | 5.25 | 55 | 6.50 | .94 |
| 10 | 4.30 | 3.00 | 60 | 6.85 | .94 |
| 15 | 4.70 | 3.00 | 70 | 7.10 | .94 |
| 20 | 5.00 | 2.25 | 80 | 7.35 | .94 |
| 25 | 5.25 | 1.87 | 90 | 7.60 | .94 |
| 30 | 5.45 | 1.50 | 100 | 7.85 | .94 |
| 35 | 5.65 | 1.50 | 110 | 8.10 | .94 |
| 40 | 6.00 | 1.50 | 120 | 8.35 | .94 |
| 45 | 6.10 | .75 | 130 | 8.60 | .94 |

¹ J. Phys. Chem., 10, 141 (1906).

by the upward trend of the curves at 65°, 75° and 85°. This result is undoubtedly due to the solvent action of the hot pyridine on the rubber, causing the membrane to be thinner at the end of the experiment than it was at the beginning. The membranes in contact with pyridine at a temperature of 85°C. were so far disintegrated at the end of 70 to 80 minutes that they would no longer sustain the column of liquid.

TABLE II
Pyridine and Water at 15°C.

| Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane | Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane |
|-----------------|-------------------------|-------------------------------------------------------------|-----------------|-------------------------|-------------------------------------------------------------|
| 0 | 5.2 | — | 65 | 11.2 | 2.25 |
| 5 | 6.6 | 10.50 | 70 | 11.5 | 2.25 |
| 10 | 7.4 | 6.00 | 75 | 11.8 | 2.25 |
| 15 | 7.9 | 3.75 | 80 | 12.1 | 2.25 |
| 20 | 8.3 | 3.00 | 85 | 12.4 | 2.25 |
| 25 | 8.7 | 3.00 | 90 | 12.7 | 2.25 |
| 30 | 9.0 | 2.25 | 100 | 13.3 | 2.25 |
| 35 | 9.3 | 2.25 | 110 | 13.9 | 2.25 |
| 40 | 9.6 | 2.25 | 120 | 14.1 | 2.25 |
| 45 | 9.9 | 2.25 | 125 | 14.5 | 2.25 |
| 50 | 10.3 | 2.25 | 130 | 15.0 | 2.40 |
| 55 | 10.6 | 2.25 | 140 | 15.5 | 2.40 |
| 60 | 10.9 | 2.25 | | | |

TABLE III
Pyridine and Water at 25°C

| Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane | Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane |
|-----------------|-------------------------|-------------------------------------------------------------|-----------------|-------------------------|-------------------------------------------------------------|
| 0 | 2.6 | — | 80 | 16.25 | 4.00 |
| 5 | 6.8 | 33.00 | 85 | 16.75 | 4.00 |
| 10 | 8.5 | 12.75 | 90 | 17.35 | 4.00 |
| 15 | 9.15 | 4.90 | 95 | 17.85 | 4.00 |
| 20 | 9.75 | 4.50 | 100 | 18.35 | 4.00 |
| 25 | 10.30 | 4.13 | 105 | 18.85 | 4.00 |
| 30 | 10.90 | 4.00 | 110 | 19.35 | 4.00 |
| 35 | 11.40 | 4.13 | 115 | 19.85 | 4.00 |
| 40 | 12.00 | 4.13 | 120 | 20.35 | 4.00 |
| 45 | 12.60 | 4.13 | 125 | 20.85 | 4.00 |
| 50 | 13.10 | 4.13 | 130 | 21.35 | 4.00 |
| 55 | 13.60 | 4.13 | 135 | 21.85 | 4.00 |
| 60 | 14.10 | 4.13 | 140 | 22.35 | 4.00 |
| 65 | 14.75 | 4.50 | 145 | 22.85 | 4.00 |
| 70 | 15.25 | 4.00 | 150 | 23.35 | 4.00 |
| 75 | 15.75 | 4.00 | | | |

TABLE IV (a)
Pyridine and Water at 35°C

| Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane | Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane |
|-----------------|-------------------------|-------------------------------------------------------------|-----------------|-------------------------|-------------------------------------------------------------|
| 0 | 2.0 | — | 85 | 20.1 | 6.00 |
| 5 | 7.2 | 39.00 | 90 | 21.7 | 6.00 |
| 10 | 8.4 | 9.00 | 95 | 22.7 | 6.00 |
| 15 | 9.3 | 6.75 | 100 | 22.7 | 6.75 |
| 20 | 10.1 | 6.00 | 105 | 23.4 | 6.00 |
| 25 | 10.9 | 6.00 | 110 | 24.2 | 6.00 |
| 30 | 11.7 | 6.00 | 115 | 25.0 | 6.00 |
| 35 | 12.6 | 6.75 | 120 | 25.8 | 6.75 |
| 40 | 13.4 | 6.00 | 125 | 26.7 | 6.00 |
| 45 | 14.2 | 6.00 | 130 | 27.5 | 6.00 |
| 50 | 15.0 | 6.00 | 135 | 28.3 | 6.00 |
| 55 | 15.9 | 6.75 | 140 | 29.0 | 5.35 |
| 65 | 16.8 | 6.75 | 145 | 29.8 | 6.00 |
| 70 | 17.6 | 6.00 | 150 | 30.6 | 6.00 |
| 75 | 18.4 | 6.00 | 155 | 31.4 | 6.00 |
| 80 | 19.3 | 6.75 | | | |

TABLE IV (b)
Pyridine and Water at 35°C

| Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane | Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane |
|-----------------|-------------------------|-------------------------------------------------------------|-----------------|-------------------------|-------------------------------------------------------------|
| 0 | 2.0 | — | 110 | 24.3 | 6.00 |
| 5 | 7.3 | 39.80 | 115 | 25.1 | 6.00 |
| 15 | 8.3 | 7.50 | 120 | 25.9 | 6.00 |
| 20 | 9.2 | 6.75 | 125 | 26.7 | 6.00 |
| 25 | 10.0 | 6.00 | 130 | 27.5 | 6.00 |
| 30 | 10.9 | 6.75 | 135 | 28.3 | 6.00 |
| 35 | 11.8 | 6.75 | 140 | 29.1 | 6.00 |
| 40 | 12.7 | 6.75 | 145 | 30.9 | 6.00 |
| 45 | 13.5 | 6.00 | 150 | 31.7 | 6.00 |
| 50 | 14.4 | 6.75 | 155 | 32.5 | 6.00 |
| 55 | 15.2 | 6.00 | 160 | 33.3 | 6.00 |
| 60 | 16.0 | 6.00 | 165 | 34.1 | 6.00 |
| 65 | 16.8 | 6.00 | 170 | 34.9 | 6.00 |
| 70 | 17.7 | 6.75 | 175 | 35.7 | 6.00 |
| 75 | 18.5 | 6.00 | 180 | 36.5 | 6.00 |
| 80 | 19.3 | 6.00 | 185 | 37.3 | 6.00 |
| 85 | 20.2 | 6.75 | 190 | 38.1 | 6.00 |
| 90 | 21.0 | 6.00 | 195 | 38.9 | 6.00 |
| 95 | 21.9 | 6.75 | 200 | 39.7 | 6.00 |
| 100 | 22.7 | 6.00 | 205 | 40.5 | 6.00 |
| 105 | 23.5 | 6.00 | | | |

TABLE V
Pyridine and Water at 45°C

| Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane | Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane |
|-----------------|-------------------------|-------------------------------------------------------------|-----------------|-------------------------|-------------------------------------------------------------|
| 0 | 1.5 | — | 80 | 26.0 | 9.00 |
| 5 | 7.3 | 43.00 | 85 | 27.2 | 9.00 |
| 10 | 8.7 | 10.50 | 90 | 28.4 | 9.00 |
| 15 | 10.0 | 9.75 | 95 | 29.5 | 8.25 |
| 20 | 11.3 | 9.75 | 100 | 30.7 | 9.00 |
| 25 | 12.6 | 9.75 | 105 | 31.9 | 9.00 |
| 30 | 14.0 | 10.50 | 110 | 33.0 | 8.25 |
| 35 | 15.2 | 9.00 | 115 | 34.2 | 9.00 |
| 40 | 16.5 | 9.75 | 120 | 35.3 | 8.25 |
| 45 | 17.7 | 9.00 | 125 | 36.4 | 8.25 |
| 50 | 18.9 | 9.00 | 130 | 37.4 | 9.00 |
| 55 | 20.0 | 8.25 | 135 | 38.4 | 8.25 |
| 60 | 21.2 | 9.00 | 140 | 39.5 | 8.25 |
| 65 | 22.4 | 9.00 | 145 | 40.6 | 7.50 |
| 70 | 23.6 | 9.00 | 150 | 41.7 | 7.50 |
| 75 | 24.8 | 9.00 | | | |

TABLE VI
Pyridine and Water at 55°C

| Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane | Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane |
|-----------------|-------------------------|-------------------------------------------------------------|-----------------|-------------------------|-------------------------------------------------------------|
| 0 | 0.50 | — | 75 | 33.00 | 12.75 |
| 5 | 8.50 | 59.50 | 80 | 34.65 | 12.00 |
| 10 | 10.45 | 14.70 | 85 | 36.25 | 12.20 |
| 15 | 12.30 | 13.85 | 90 | 37.90 | 12.20 |
| 20 | 14.15 | 13.85 | 95 | 39.50 | 12.20 |
| 25 | 15.95 | 13.50 | 100 | 41.10 | 12.50 |
| 30 | 17.75 | 13.50 | 105 | 42.90 | 12.70 |
| 35 | 19.55 | 13.50 | 110 | 44.40 | 11.90 |
| 40 | 21.30 | 13.10 | 115 | 46.40 | 12.70 |
| 45 | 23.00 | 12.70 | 120 | 47.90 | 12.70 |
| 50 | 24.70 | 13.10 | 130 | 51.50 | 12.70 |
| 55 | 26.35 | 12.00 | 140 | 55.10 | 13.40 |
| 60 | 28.00 | 12.35 | 150 | 58.50 | 12.70 |
| 65 | 29.80 | 12.40 | 160 | 63.80 | 12.70 |
| 70 | 31.35 | 12.40 | 170 | 65.50 | 12.70 |

TABLE VII
Pyridine and Water at 65°C

| Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane | Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane |
|-----------------|-------------------------|-------------------------------------------------------------|-----------------|-------------------------|-------------------------------------------------------------|
| 0 | 0.40 | — | 95 | 52.40 | 16.50 |
| 5 | 11.00 | 79.50 | 100 | 54.60 | 16.50 |
| 10 | 13.80 | 21.00 | 105 | 56.80 | 16.50 |
| 15 | 16.40 | 19.50 | 110 | 59.00 | 16.50 |
| 20 | 18.70 | 17.20 | 115 | 61.30 | 17.20 |
| 25 | 21.00 | 17.20 | 120 | 63.50 | 16.50 |
| 30 | 23.30 | 17.20 | 130 | 69.00 | 16.90 |
| 35 | 25.50 | 16.50 | 140 | 72.60 | 17.30 |
| 40 | 27.80 | 17.20 | 150 | 77.30 | 17.60 |
| 45 | 30.10 | 17.20 | 155 | 79.60 | 17.20 |
| 50 | 32.40 | 17.20 | 160 | 81.90 | 17.20 |
| 55 | 34.70 | 17.20 | 165 | 84.20 | 17.20 |
| 60 | 37.00 | 17.20 | 170 | 86.50 | 17.20 |
| 65 | 39.30 | 17.20 | 175 | 88.80 | 17.20 |
| 70 | 41.50 | 16.50 | 180 | 90.30 | 17.20 |
| 75 | 43.70 | 16.50 | 185 | 95.80 | 20.60 |
| 80 | 45.90 | 16.50 | 190 | 98.20 | 18.00 |
| 85 | 48.10 | 16.50 | 195 | 100.30 | 18.70 |
| 90 | 50.20 | 15.60 | 200 | 102.10 | 18.70 |

TABLE VIII
Pyridine and Water at 75°C

| Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane | Time in minutes | Total cms. rise in tube | Vol. in passing through 1 cm. ² membrane |
|-----------------|-------------------------|-------------------------------------------------------------|-----------------|-------------------------|-----------------------------------------------------|
| 0 | 2.1 | — | 50 | 39.5 | 22.0 |
| 5 | 13.1 | 82.5 | 55 | 42.5 | 23.6 |
| 10 | 16.7 | 28.3 | 60 | 45.6 | 22.7 |
| 15 | 20.0 | 24.6 | 70 | 51.8 | 22.7 |
| 20 | 22.9 | 23.4 | 75 | 55.0 | 23.4 |
| 25 | 25.5 | 22.6 | 80 | 58.1 | 22.6 |
| 30 | 28.2 | 23.0 | 85 | 61.3 | 23.4 |
| 35 | 31.0 | 24.0 | 90 | 64.5 | 23.4 |
| 40 | 33.8 | 24.0 | 95 | 67.8 | 24.0 |
| 45 | 36.6 | 22.6 | | | |

TABLE IX
Pyridine and Water at 85°C

| Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane | Time in minutes | Total cms. rise in tube | Vol. in cu. mm. passing through 1 cm. ² membrane |
|-----------------|-------------------------|-------------------------------------------------------------|-----------------|-------------------------|-------------------------------------------------------------|
| 0 | 3.0 | — | 40 | 48.9 | 28.5 |
| 5 | 19.0 | 120.0 | 45 | 52.5 | 27.0 |
| 10 | 24.7 | 43.6 | 50 | 56.3 | 28.5 |
| 15 | 29.3 | 34.2 | 55 | 60.0 | 27.8 |
| 20 | 33.4 | 30.8 | 60 | 63.8 | 28.5 |
| 25 | 37.2 | 28.5 | 65 | 67.8 | 30.0 |
| 30 | 41.0 | 28.5 | 70 | 72.0 | 31.4 |
| 35 | 45.1 | 30.8 | | | |

Experiments showing the Effect of Temperature Changes on the Passage of Sodium Chloride from a One-half Molar Solution through a Collodion Membrane into Water.

The sodium chloride was purified by precipitation with hydrogen chloride. The water was distilled and had been boiled to free it from dissolved gases. The collodion sack was prepared by pouring an alcohol-ether solution of nitrocellulose into a large test tube, rotating the tube and draining out the excess solution. After a short time had elapsed the membrane was removed from the tube and washed thoroughly in distilled water. The membrane was perfectly transparent.

A large cork stopper which had a large hole cut in the center and which had been thoroughly covered on its entire surface with collodion was fitted into the mouth of the sack. The sack itself was 13 centimeters long and 4 centimeters in diameter. When 100cc. of solution were placed in the sack 85 square centimeters of surface were presented for dialysis.

The bag was suspended in a one and one-half liter beaker by means of a wire clamp attached to the cork and fitted over the side of the beaker. The beaker was immersed in the same thermostat used in the experiments with rubber membranes. A glass stirrer passed through the hole in the cork stopper and effectively agitated the contents of the sack. Another stirrer circulated the contents of the beaker. 100cc. of the salt solution were placed in the bag and 1200cc. of distilled water in the beaker. The solution and the water in the beaker were both brought to the temperature of the thermostat before lowering the sack into the water.

10cc. samples were drawn every 5 minutes from the beaker. The contents of the beaker were agitated with a current of air just before drawing each sample. This was done to make certain that there was not a layer of concentrated solution at the bottom of the beaker which had not been completely eliminated by the action of the mechanical stirrer. 10cc. of pure water at the temperature of the experiment were added for every 10cc. of solution withdrawn. Corrections were made for this continual dilution.

The chloride was determined in each sample drawn by means of a N/100 solution of silver nitrate, using potassium chromate as indicator.

Experiments were performed at ten-degree intervals from 25°C to 65°C. Two or more experiments were conducted at each temperature and it was found possible to check within small margins between two runs at the same temperature. The quantity of salt in the system at the end of a run as calculated from the analytical results checked the amount in the original 100cc.

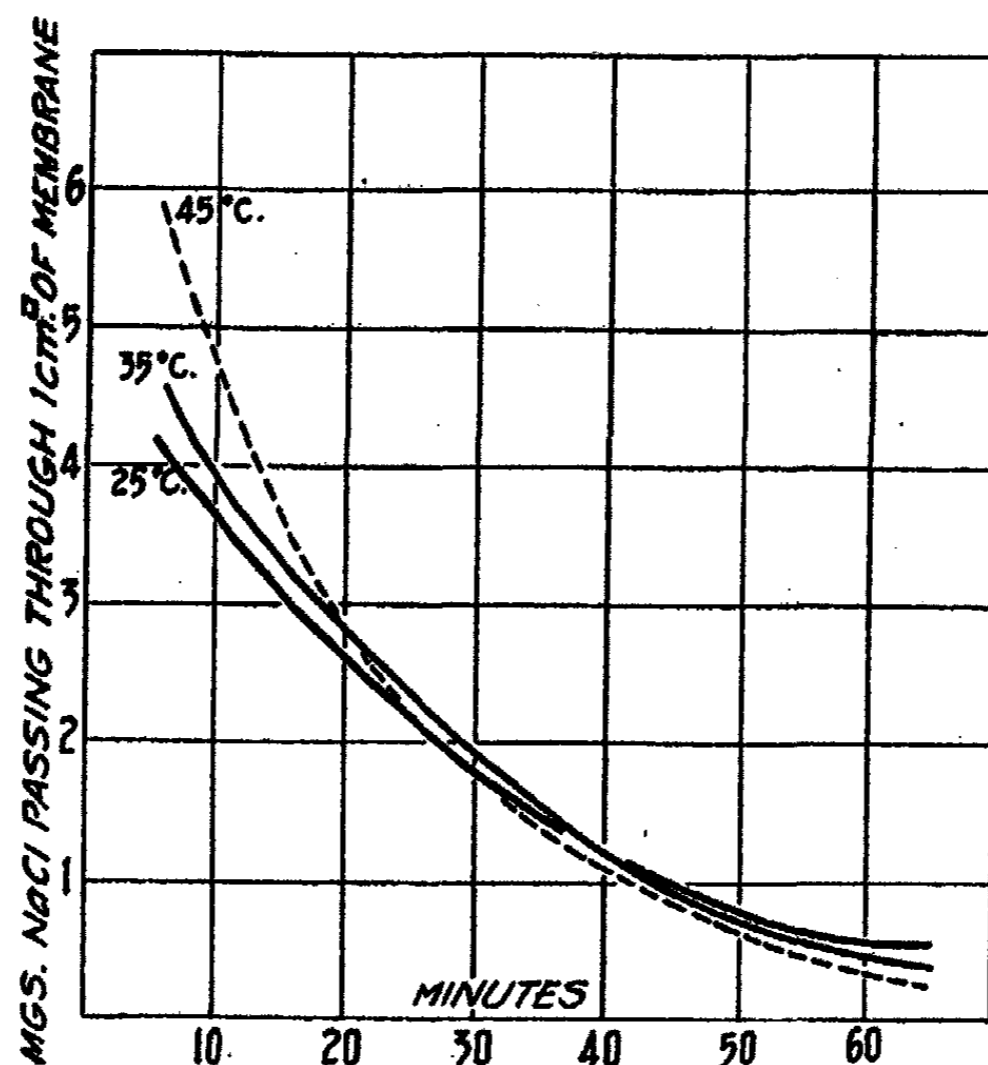


FIG. 3

of a one-half molar solution within 0.15% to 0.20%. When the transfer of sodium chloride became almost zero the contents of the sack in each experiment measured approximately 110cc. indicating a flow of water through the collodion membrane toward the salt solution.

The same membrane was used for the first seven runs. This membrane was accidentally broken and a new one had to be prepared. To determine whether results from two different membranes were comparable, some of the determinations made with the first membrane were repeated with the new one. These determinations checked almost as closely as those made with the same membrane. It is thus possible to prepare two collodion membranes from the

same material and following the same procedure which will show the same rate of permeability to a soluble salt such as sodium chloride. It should be noted at this point that the membranes were soaked thoroughly in distilled water between experiments.

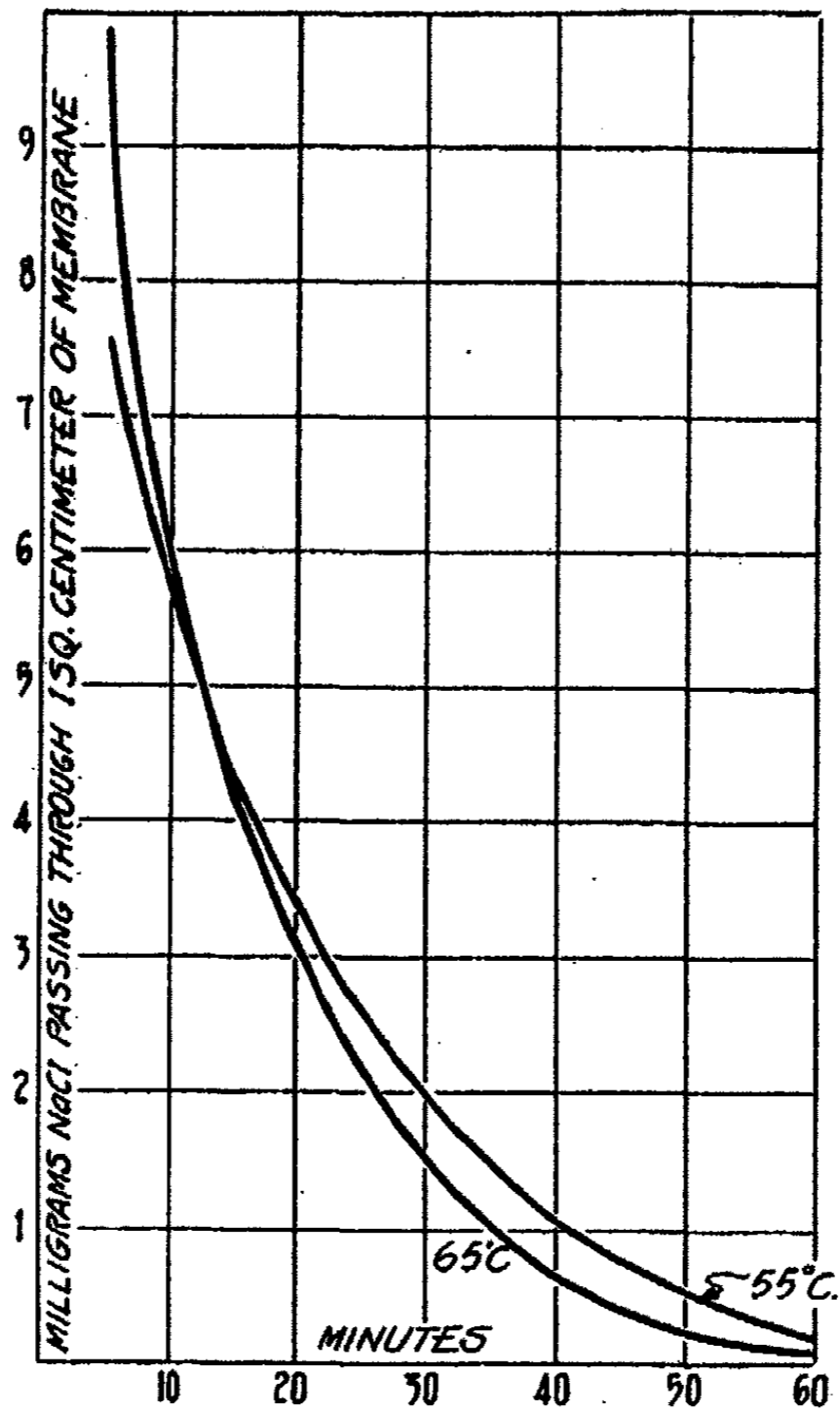


FIG. 4

The amount of sodium chloride in milligrams passing through one square centimeter of the collodion membrane in five minutes was calculated from the analytical data. These are the values given in column three of Tables X to XIV and used in plotting against time in Figs. 3 and 4.

TABLE X
NaCl through Collodion at 25°C

| Time in minutes | cc. 1/100 N AgNO ₃ required for NaCl entering 100.c. in five minutes | Mgs. NaCl passing through 1 cm. ² of membrane in 5 min. | Time in minutes | cc. 1/100 N AgNO ₃ required for NaCl entering 100.c. in five minutes | Mgs. NaCl passing through 1 cm. ² of membrane in 5 min. |
|-----------------|---------------------------------------------------------------------------------|--------------------------------------------------------------------|-----------------|---------------------------------------------------------------------------------|--------------------------------------------------------------------|
| 5 | 4.90 | 4.20 | 50 | 1.10 | .95 |
| 10 | 4.25 | 3.66 | 55 | 1.00 | .86 |
| 15 | 3.50 | 3.02 | 60 | .70 | .61 |
| 20 | 2.90 | 2.47 | 65 | .70 | .61 |
| 25 | 2.20 | 1.86 | 70 | .50 | .44 |
| 30 | 2.00 | 1.73 | 75 | .60 | .51 |
| 35 | 1.60 | 1.39 | 80 | .60 | .51 |
| 40 | 1.35 | 1.29 | 85 | .45 | .39 |
| 45 | 1.20 | 1.04 | 90 | .40 | .35 |

TABLE XI
NaCl through Collodion at 35°C

| Time in minutes | cc. 1/100 N AgNO ₃ required for NaCl entering 100.c. in five minutes | Mgs. NaCl passing through 1 cm. ² of membrane in 5 min. | Time in minutes | cc. 1/100 N AgNO ₃ required for NaCl entering 100.c. in five minutes | Mgs. NaCl passing through 1 cm. ² of membrane in 5 min. |
|-----------------|---------------------------------------------------------------------------------|--------------------------------------------------------------------|-----------------|---------------------------------------------------------------------------------|--------------------------------------------------------------------|
| 5 | 5.40 | 4.65 | 50 | 1.00 | .86 |
| 10 | 4.85 | 4.18 | 55 | .80 | .59 |
| 15 | 4.10 | 3.65 | 60 | .60 | .52 |
| 20 | 3.10 | 2.67 | 65 | .50 | .41 |
| 25 | 2.65 | 2.28 | 70 | .50 | .41 |
| 30 | 2.10 | 1.83 | 75 | .40 | .34 |
| 35 | 1.80 | 1.52 | 80 | .50 | .41 |
| 40 | 1.60 | 1.37 | 85 | .50 | .41 |
| 45 | 1.20 | 1.03 | | | |

TABLE XII
NaCl through Collodion at 45°C

| Time in minutes | cc. 1/100 N AgNO ₃ required for NaCl entering 100.c. in five minutes | Mgs. NaCl passing through 1 cm. ² of membrane in 5 min. | Time in minutes | cc. 1/100 N AgNO ₃ required for NaCl entering 100.c. in five minutes | Mgs. NaCl passing through 1 cm. ² of membrane in 5 min. |
|-----------------|---------------------------------------------------------------------------------|--------------------------------------------------------------------|-----------------|---------------------------------------------------------------------------------|--------------------------------------------------------------------|
| 5 | 7.05 | 6.10 | 45 | 1.45 | 1.25 |
| 10 | 5.70 | 4.90 | 50 | .90 | .78 |
| 15 | 4.20 | 3.61 | 55 | .70 | .60 |
| 20 | 3.20 | 2.74 | 60 | .50 | .43 |
| 25 | 2.75 | 2.37 | 65 | .50 | .43 |
| 30 | 2.35 | 2.00 | 70 | .60 | .52 |
| 35 | 1.75 | 1.51 | 75 | .40 | .34 |
| 40 | 1.35 | 1.07 | 80 | .30 | .26 |

TABLE XIII
NaCl through Collodion at 55°C

| Time in minutes | c.c. 1/100 N AgNO ₃ required for NaCl entering 100.c. in five minutes | Mgs. NaCl passing through 1 cm. ² of membrane in 5 min. | Time in minutes | c.c. 1/100 N AgNO ₃ required for NaCl entering 100.c. in five minutes | Mgs. NaCl passing through 1 cm. ² of membrane in 5 min. |
|-----------------|----------------------------------------------------------------------------------|--------------------------------------------------------------------|-----------------|----------------------------------------------------------------------------------|--------------------------------------------------------------------|
| 5 | 9.0 | 7.77 | 35 | 1.6 | 1.38 |
| 10 | 7.2 | 6.17 | 40 | 1.2 | 1.03 |
| 15 | 4.6 | 3.98 | 45 | .8 | .68 |
| 20 | 3.8 | 3.30 | 50 | .6 | .50 |
| 25 | 2.8 | 2.40 | 55 | .4 | .34 |
| 30 | 2.0 | 1.72 | 60 | .2 | .18 |

TABLE XIV
NaCl through Collodion at 65°C

| Time in minutes | c.c. 1/100 N AgNO ₃ required for NaCl entering 100.c. in five minutes | Mgs. NaCl passing through 1 cm. ² of membrane in 5 min. | Time in minutes | c.c. 1/100 N AgNO ₃ required for NaCl entering 100.c. in five minutes | Mgs. NaCl passing through 1 cm. ² membrane in 5 mins. |
|-----------------|----------------------------------------------------------------------------------|--------------------------------------------------------------------|-----------------|----------------------------------------------------------------------------------|------------------------------------------------------------------|
| 5 | 11.6 | 10.00 | 35 | 1.4 | 1.20 |
| 10 | 7.3 | 6.27 | 40 | .6 | .52 |
| 15 | 5.0 | 4.30 | 45 | .3 | .26 |
| 20 | 3.2 | 2.75 | 50 | .3 | .26 |
| 25 | 2.5 | 2.18 | 55 | .2 | .18 |
| 30 | 1.8 | 1.56 | 60 | 0 | .00 |

Discussion

The rate of passage of pyridine through thin rubber membranes increases with rise in temperature. Approximately, the velocity at 15°C is double that at 5°C and at 25°C it is twice as much as at 15°C. At 35°C the rate is 50 percent greater than at 25°C and the velocity at 45°C is also 50 percent greater than at 35°C. The rate at 55°C is 33 percent greater than at 45°C and at 65°C it is one third larger than at 55°C. The increase between 65° and 75°C and between 75°C and 85°C appears to lie in the neighborhood of 33 to 25 percent.

Any explanation of such experimental results is necessarily rather speculative. The ideas of Armstrong¹ and Gillet² offer a rather attractive explanation of the observed results. Water is considered as an equilibrium mixture of hydrol (H₂O), dihydrol (H₂O)₂ and polyhydrol (H₂O)_n. The equilibrium between these forms is affected by temperature; the higher the temperature the greater the amount of hydrol (H₂O) present. This "monad" is very reactive

¹ Proc. Roy. Soc., 78A, 264 (1906).

² Compt. rend., 177, 257 (1923).

and is chiefly responsible for the chemical activities of water. The introduction of foreign materials into water which are soluble in the liquid tend also to disturb the equilibrium in the direction $(H_2O)_n \rightarrow nH_2O$.

At the lower temperatures the amount of (H_2O) present is relatively small. It is this hydrol (H_2O) which attracts the pyridine and removes it from the surface of the rubber membrane. It would appear from the data given above that from $5^\circ C$ to $25^\circ C$ the production of (H_2O) under the influence of temperature is regular and about doubles for each 10 degree increase provided the attraction of water for pyridine may be taken as a measure of the amount of hydrol present. Above $25^\circ C$ the relative effect of temperature on hydrol formation (and attraction of water for pyridine) becomes less; up to $45^\circ C$ being about a 50 percent increase for each 10 degree interval and from there up to $65^\circ C$ showing a 33 percent increase for a like interval. Above $65^\circ C$ the amount of hydrol (H_2O) present in the equilibrium mixture is so large that an increase in temperature has relatively less effect.

The uniformity of the rates for temperatures from 5° to $65^\circ C$ after the first 30 minutes may be explained by the fact that sufficient pyridine has entered by that time to combine with the hydrol originally present. The dihydrol and polyhydrol present are continually dissociating under the effects of the temperature of the experiment. The hydrol thus liberated combines immediately with pyridine and the dissociation continues, the rate being governed by the temperature. An excellent example of this was shown in an experiment not recorded above which was allowed to run at $25^\circ C$ for seven and one-half hours. No material change in rate was noted over the last seven hours of the experiment.

At the high temperatures, 75° and $85^\circ C$, complications arise because of the vigorous action of the hot pyridine on the rubber. The membranes gave way entirely after exposure to pyridine at $85^\circ C$ for 70 to 80 minutes. It is evident, however, that increase in temperature at these higher levels would have relatively less effect. The equilibrium mixture would contain a preponderance of hydrol with some dihydrol and relatively little polyhydrol, consequently a temperature change would have a smaller effect on the production of (H_2O) in proportion to the amount originally present than would a like change at a lower temperature where less hydrol and more of its polymers were present in the original equilibrium mixture.

The above reasoning ignores the effect of the membrane on the rate of passage of the pyridine through it. This factor is one that must be recognized. Pyridine dissolves in rubber and the water (hydrol, H_2O) on the upper side of the rubber removes the pyridine from the surface. Increase in temperature increases the solubility of pyridine in rubber so that the effect of the membrane in this particular case tends to be in the same direction as the other effects mentioned above.

In the case of the passage of sodium chloride from an aqueous solution through a collodion membrane into water it is more difficult to draw conclusions. There is transfer in both directions because water passes through the collodion membrane into the salt solution at the same time that the salt

passes through into the water. In other words the membrane in this system is not at all semipermeable. Equilibrium tends to be established with the concentration of the salt the same on both sides of the membrane. The higher the temperature the more rapidly the salt passes through the membrane *at first* but the rate of passage is very nearly the same for all temperatures between 25°C and 65°C at the end of 30 minutes.

Summary

1. The volumes of pyridine in cubic millimeters passing through one square centimeter of rubber dam into pure water at temperature intervals of 10 degrees from 5°C to 85°C were determined.
2. The rate increases 100 percent for 10 degree intervals between 5°C and 25°C; 50 percent between 25°C and 45°C; 33 percent between 45°C and 65°C; and from 33 to 25 percent for 10 degree intervals between 65°C and 85°C.
3. The milligrams of sodium chloride from a one-half molar aqueous solution passing through one square centimeter of collodion membrane into water were determined for 10 degree temperature intervals between 25°C and 65°C.
4. The *initial* rate of passage of the salt through collodion is greater the higher the temperature, but the rate is practically the same for all temperatures at the end of 30 minutes of dialysis.
5. The reasons for the results obtained in the experiments on pyridine are discussed from the viewpoint of the theory that water is an equilibrium mixture of hydrol (H₂O) and its polymers.

The author wishes to express his indebtedness to Mr. Harry N. Huntzicker for his assistance in the experimental work on the pyridine-rubber-water system.

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GALLIUM. I. ARC SPECTROGRAPHIC DETECTION AND ESTIMATION OF GALLIUM. II. EXTRACTION OF GALLIUM FROM LEPIDOLITE¹

BY JACOB PAPISE AND DONALD A. HOLT

I. Arc Spectrographic Detection and Estimation of Gallium

General. Arc spectroscopy is well suited to the needs of the analytical chemist. When the visible and the ultraviolet spectral ranges are considered it will be noticed that the great majority of metals and a number of non-metals have their persistent lines in these ranges. Arc spectra, as a rule, are intense and this makes them especially adaptable to spectrographic observation. If the substance to be analyzed is a good conductor of electricity, such as a metal or an alloy, and is in the form of wire or rod, it can be used directly as electrode material. Ordinarily the chemist is confronted with the handling of substances that are non-conductors; even in the case of metals he has to work frequently with granules, powders, borings and lumps which cannot be made into electrodes, at least, not conveniently. In such cases and also in the case of liquids, use is made of graphite rods of suitable diameter and length to hold the substances to be subjected to spectral excitation. Artificial graphite of a very high degree of purity is procurable for spectroscopic work. When an arc is made between two such graphite rods, the spectrum will be found to contain, in addition to the lines and bands due to carbon and to some of its compounds, also lines due to a number of impurities such as magnesium, sodium, calcium, lithium, silicon, iron and manganese. Other things being equal, the intensity and the number of these lines will depend upon the quantities of the respective impurities.

The direct current is used for the production of the arc, and it is the practice to make the lower electrode the anode. The anode is considerably hotter than the cathode. This fact can be observed any time on breaking the arc: the anode will be red-hot over a longer distance and it will continue to glow some time after the cathode has become dark. When the lower electrode is made the anode, and the substance to be analyzed is placed on it, it will be observed that the spectroscopic test, in a great many cases, is much more sensitive than in the event of reversed polarity.

A quartz spectrograph fitted with one Cornu prism, or a larger auto-collimating Littrow type of instrument, is suitable for work in the ultraviolet region. The latter instrument gives very good results also in the visible range. For the detection of gallium which has persistent lines in the visible, a glass instrument can be used. Ordinary photographic plates with a sensitivity between λ 5000 and λ 2350 give very good results, and of course special plates should be used for ranges other than this. The method of developing

¹The experimental work described in this article was made possible through a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

and fixing is similar to the one followed in ordinary photographic work with one outstanding difference: In spectrography the chemist is after hardest contrasts obtainable.

Experimental Work with Gallium. Freshly precipitated gallium hydroxide, which on spectrographic examination was found to contain only negligible traces of sodium, iron, calcium, magnesium and silicon, was converted to the chloride with the aid of hydrochloric acid. The gallium content of this solution was determined gravimetrically and water was added to bring the concentration to 0.1 percent. From this stock solution, solutions containing 0.01, 0.001 and 0.0001 gm. of gallium per 100 cc. were prepared. A small, definite portion (0.1 cc.) of each solution, delivered from a graduated capillary pipette, was placed on the lower graphite electrode and subjected to arc excitation. These portions contained 0.1, 0.01, 0.001 and 0.0001 mg. of gallium respectively. Fresh electrodes were used in connection with each test. The spectral lines observed at the different concentrations are recorded in Table I.

TABLE I

| λ | 0.1 mg. | 0.01mg. | 0.001mg. | 0.0001mg. |
|-----------|---------|---------|----------|-----------|
| 4172.0 | v | v | vf | |
| 4033.0 | v | v | vf | |
| 2944.2 | v | v | f | |
| 2943.6 | v | v | v | f |
| 2874.2 | v | v | v | f |
| 2719.7 | v | v | vf | |
| 3659.9 | v | v | vf | |
| 2500.2 | v | v | vf | |
| 2450.1 | v | f | | |
| 2338.6 | vf | | | |

Note. "v" designates the fact that the line is visible, "f", that it is faint and "vf" that it is very faint.

If gallium in quantities larger than 0.1 mg. be arced, the following spectral lines, in addition to those given in Table I will be observed: 3020.5, 2418.7, 2371.3, and 2249.2. Because the human eye is much more sensitive to visible radiation than the photographic plate, λ 4172.0 and λ 4033.0 are visible when the concentration of gallium is lower than the lowest given in the table. This is especially true of the lower frequency line. The gallium line 2874.2 is coincident with an iron line of practically the same wave length. It should be borne in mind, however, that this iron line is of low persistence, and if it is visible, many other lines due to this element should be present.

Fifty-five minerals were examined spectrographically for the presence of gallium. The observations are recorded in Table II. The term *trace* as employed in this table designates quantities in the neighborhood of 0.001%; *large trace*, stands for quantities in the neighborhood of 0.01% and *small trace* for quantities less than 0.001%. To illustrate how these have been arrived at, the case of lepidolite (from San Bernardino County, California) will be briefly considered.

TABLE II

| Mineral | Place of origin | Ga content |
|---------------------|---------------------------------------|-------------|
| Albite | Bedford, New York | Trace |
| Albite | Richville, New York | Small trace |
| Alunite | Marysvale, Utah | Absent |
| Analoite | Table Mountain, Golden, Colorado | Small trace |
| Apatite | Buckingham, Quebec | Absent |
| Ball clay | Tennessee | Small trace |
| Bauxite | Linnwood, Georgia | Small trace |
| Bauxite | Bauxite, Arkansas | Absent |
| Beryl | South Australia | Absent |
| Beryl | Bedford, New York | Absent |
| Beryl | Canada | Small trace |
| Chlorite | Putnam County, New York | Absent |
| Corundum | Iredell County, North Carolina | Small trace |
| Emery | Peekskill, New York | Small trace |
| Enargite | Chiapas, Mexico | Absent |
| Feldspar | Quebec, Canada | Trace |
| Franklinite | Franklin Furnace, New Jersey | Absent |
| Garnet | Franklin Furnace, New Jersey | Absent |
| Garnet | Warren County, New York | Absent |
| Indiananite | Huron, Indiana | Absent |
| Kaolin | Holly Springs, Pennsylvania | Small trace |
| Kunzite | Palo County, California | Trace |
| Labradorite | St. John County, Quebec | Trace |
| Labradorite | Maine, Labrador | Trace |
| Lazurite | Andes de Ovalle, Chile | Small trace |
| Lepidolite | San Bernardino County, California | Large trace |
| Lepidolite | Oxford County, Maine | Trace |
| Leucite | Albeno, Italy | Small trace |
| Lithiophyllite | Black Hills, South Dakota | Absent |
| Microcline | El Paso County, California | Large trace |
| Microcline | Verona, Ontario | Trace |
| Microcline | Franklin Furnace, New Jersey | Trace |
| Microcline | Chestnut Flat Mine, North Carolina | Trace |
| Microcline | Godfrey, Ontario | Trace |
| Microcline | Davis Mine, New Hampshire | Trace |
| Microcline | Virginia | Large trace |
| Muscovite | Asheville, North Carolina | Trace |
| Natroloite | Medford, Oregon | Trace |
| Nephelite | Bancroft, Ontario | Trace |
| Oligoclase | Orange County, New York | Trace |
| Orthoclase | Quebec | Small trace |
| Orthoclase (pebble) | Pacific Grove, California | Trace |

TABLE II (Continued)

| Mineral | Place of origin | Ga content |
|------------|--------------------------------|-------------|
| Sodalite | Litchfield, Maine | Small trace |
| Sodalite | Hastings County, Ontario | Small trace |
| Spodumine | California | Trace |
| Stilbite | Peekskill, New York | Absent |
| Stilbite | West Paterson, New Jersey | Absent |
| Tourmaline | El Paso County, California | Large trace |
| Tourmaline | San Diego County, California | Large trace |
| Tourmaline | Winter Harbor, Maine | Trace |
| Tourmaline | Richland, New York | Trace |
| Tourmaline | Bedford, New York | Trace |
| Turquoise | New Mexico | Absent |
| Wavellite | Montgomery County, Arkansas | Absent |
| Willemite | Franklin Furnace, New Jersey | Absent |

Finely powdered lepidolite in five and ten milligram portions was subjected to arc excitation. The spectrograms in the case of the higher quantity contained the gallium lines 4172.0, 4033.0, 2944.2 (faint), 2943.6 and 2874.2. This would seem to indicate that a quantity higher than 0.001 mg. and lower than 0.01 mg. of gallium was present in the zone of excitation. Expressed in percentages, the gallium content is estimated to be between 0.001 and 0.01. The shortcomings of this method of estimating the quantity of an element are obvious: The reactions in the arc are beyond the control of the operator. However, if the limits are wide, it is possible in many cases to differentiate between traces and larger quantities, especially if the element has spectral lines of great sensitivity.

II. Extraction of Gallium from Lepidolite

The mineral, ground to pass through a 40 mesh sieve, was fused in a nickel crucible with twice its weight of potassium hydroxide, and while still in a pasty condition, the fused mass was broken up in small particles by stirring with an iron rod. It was transferred to a tall glass cylinder containing water, stirred with a current of air and allowed to settle. The supernatant liquid was siphoned off, more water was poured in the cylinder, stirred as before; the solid was again allowed to settle and the liquid was removed. This was repeated till about ten liters of water were used for one kilogram of original mineral. The residue which contained practically all the aluminum and all the gallium, a fact established spectroscopically, was placed in an evaporator, treated with concentrated hydrochloric acid and heated to "crack" the silica gel. The aluminum and gallium were extracted with successive portions of dilute hydrochloric acid and the extraction was deemed completed when the residual silica showed no gallium or the merest traces when examined spectroscopically. The chloride solution was concentrated to a small volume

and the excess of mineral acid was neutralized with ammonium acetate and an excess of acetic acid was added. Potassium arsenite was added to this and the whole was first saturated with sulphur dioxide to make sure that the arsenic is in the trivalent state, and next with hydrogen sulphide. The galliferous arsenious sulphide was removed by filtration. But the filtrate was not entirely free from gallium, and in order to recover this fraction it was necessary to repeat the procedure of adding potassium arsenite and saturating with sulphur dioxide and with hydrogen sulphide until a precipitate of arsenious sulphide was obtained which did not carry gallium. The galliferous precipitates were transferred to an evaporator and treated with nitric acid. The unoxidized sulphur was removed by filtration and washed till it was found to be free from gallium. The excess of nitric acid in the filtrate was driven off by evaporation and hydrochloric acid was added. The solution was saturated with sulphur dioxide and with hydrogen sulphide and the precipitated arsenious sulphide was removed by filtration. It was found on spectroscopic examination that even this residue on careful washing with hydrochloric acid retained minute traces of gallium. The filtrate which contained aluminum and gallium was concentrated to a small volume, made strongly acid with hydrochloric acid and an excess of potassium ferrocyanide was added to it. This brought about the precipitation of gallium as the ferrocyanide together with a comparatively large quantity of ferrocyanic acid. Since gallium ferrocyanide, like other ferrocyanides, is peptized by adsorption of the ferrocyanide ion, it was found necessary to employ egg albumin to facilitate the removal of the solids by filtration. The residue thus obtained was washed on the filter with dilute, warm hydrochloric acid until washings gave no test for aluminum. The residue and filter were ignited. Aqua regia was added and heat applied until complete solution was brought about. Successive portions of hydrochloric acid were next added and driven off by evaporation to insure the removal of the oxides of nitrogen. The hydrochloric acid in turn was neutralized with ammonium acetate; acetic acid was added and the iron was precipitated out by adding a freshly prepared hot solution of α -nitroso- β -naphthol in 50% acetic acid. The iron precipitate, when separated from the solution and washed on the filter, was found on spectroscopic examination to be free from gallium. The filtrate was made alkaline with ammonium hydroxide and boiled until gallium hydroxide precipitated out. This was removed by filtration, washed and ignited to the oxide. A spectrographic examination of the freshly precipitated gallium hydroxide proved that it contained negligible traces of the commoner elements ordinarily associated with substances of highest purity. The ignited oxide contained the same impurities, especially silicon and magnesium, to a somewhat higher degree. These, evidently, were derived from the incinerated filter paper.

One kilogram of lepidolite treated in the manner just described yielded 0.0887 gm. of Ga_2O_3 . The gallium content of the mineral expressed as percentage is very close to 0.007.

Summary

A method for the arc spectrographic detection and estimation of gallium was described.

Fifty-five minerals were examined spectrographically for the presence of gallium and the results recorded.

A method for the extraction of gallium from lepidolite was described.

Cornell University.

NEW BOOKS

Recent Advances in Organic Chemistry. Vols. I and II. By Alfred W. Stewart. Fifth edition. 22 × 15 cm; Vol. I, pp. xiv + 357; Vol. II, pp. xiv + 352. London and New York: Longmans, Green and Co., 1927. Price: \$7.50. The first volume contains "a survey of numerous fundamental problems of organic chemistry, and, with some few exceptions, it deals with subjects upon which general agreement has now been reached." The chapters are entitled: some main currents in organic chemistry; sundry modern reagents; addition reactions; the aliphatic diazene compounds; the ketens; the polyketides and their allies; the monocyclic terpenes; the dicyclic terpenes; the olefinic terpenes; the pyrrol, pyridine, and tropine alkaloids; the quinoline and isoquinoline alkaloids; the purine group; the polypeptides; trivalent carbon; unsaturation; orienting influences in the benzene system; conclusion.

"In every science which is at all progressive there must arise from time to time conflicts between the older generation of workers and the leaders of the new; for, to those who have grown up along with it, a theory generally becomes invested with a sanctity which is quite out of keeping with its true make-shift character. The longer a theory stands, the harder it is to shake it, and the greater is the tendency to become stereotyped. There is another side to the matter. Without any disrespect, it may be said that the majority of scientific investigators are not possessed of strikingly original minds—we cannot all be Pasteurs—and hence there is a pronounced tendency to take things as they are and work along the beaten track rather than to push out in the wilderness and risk the chance of losing the road altogether. Thus round every theory there grows up a little band of workers, whose one aim seems to be to accumulate evidence confirming their favorite hypothesis; and in this way the theory gains considerable weight of supporting data. On the other hand, the solitary worker who happens to differ from the majority of his fellows has to overcome a tremendous weight of unconscious prejudice before he is able to obtain even the semblance of an impartial hearing. In spite of these difficulties, however, progress is made," p. 1.

"When the recent progress of organic chemistry is compared with the tremendous revolutions in inorganic chemistry and radioactivity which have been brought about by the work of Thomson, Ramsay, Rutherford, Soddy, Aston, and Lewis, the contrast cannot but strike the mind.

"One reason for this comparative barrenness is perhaps to be found in the attraction which the newer subjects have exercised upon investigators, drawing the more original minds away from organic problems. The formula of triphenylmethane is certainly a less entrancing subject than, say, the peculiar phenomenon of isosterism; and it is only natural that inquiring intellects should concentrate themselves by preference upon matters which seem more fundamental than problems of molecular structure.

"There is, however, no reason to despair of the future of organic chemistry. It is true that the mere synthesis of a large number of new substances or even the clearing-up of the constitution of some intricate alkaloid will not lead to a fresh avatar of the subject. What is urgently needed is a completely new line of development. It is not difficult to suggest ways in which such a change of trend might be accomplished. For example, nine-tenths at least of our laboratory reactions lie outside the temperature-limits under which the plants and the animals exist, yet plants and animals succeed in producing quite considerable yields of certain materials which we can obtain in the laboratory only with some difficulty. It seems not impossible that a study of reactions which can take place at ordinary temperatures and in the absence of violent reagents, might open up an entirely fresh line of development in organic chemistry. Our increased modern knowledge of catalysts and their action makes this field much more promising than it once was; and the possibilities involved in the use of colloidal reagents need only be mentioned in order to suggest lines of investigation which could hardly prove unfruitful," p. 17.

"Although the word "alkaloid" is one of the best known in chemical terminology, an exact definition of its meaning is by no means simple. For present purposes, a general idea of alkaloidal character is more important than an academic definition; and the following description will suffice here.

"The alkaloids are naturally-occurring nitrogen compounds which possess certain specific physiological actions upon animal organisms. Thus atropine has a mydriatic effect and is used for expanding the pupil of the eye; quinine is employed as a febrifuge to reduce temperature during fever; strychnine produces the muscular effects noticed in cases of strychnine poisoning; and cocaine acts as a local anaesthetic. In the majority of alkaloids, but not in all, the nitrogen atom is a member of a ring-system such as pyrrol, pyridine, or quinoline; and even in cases where it is a part of an open chain it is either secondary or tertiary in character. In consequence, the majority of alkaloids have basic characteristics; but this is not an invariable rule, since some of the purine group are acidic in their nature.

"On examination of the more familiar alkaloids it is found that they are built up on the basis of the pyridine ring, just as the aromatic compounds are founded on the benzene nucleus; and as among aromatic types a benzene ring is sometimes found to be condensed with other cyclic chains, so in the pyridine alkaloids there are compounds wherein the pyridine ring is overlaid with others, yielding derivatives of quinoline or isoquinoline," p. 205.

"The main characteristics of the polypeptide class may now briefly be summarized, and it is of interest to compare them with those of the naturally occurring proteins. The polypeptides are solids, which usually melt at about 200°C, with some decomposition. They are easily soluble in water, but insoluble in alcohol, like some of the albumins; and instead of having the usual insipid or sweet taste of the ordinary amino-acid, they are bitter, like the protein derivatives. In dilute sulphuric acid solution they are precipitated by phosphotungstic acid, in which behavior they resemble the albumins. Both the natural and artificial classes give the biuret reaction. The action of ferments, or of acids or alkalis, is the same in both classes; and similar products are obtained when animals are fed with polypeptides and albumins. In the case of ferment action it is found that much depends upon the groups which have been used in building up the polypeptide structure, some polypeptides being much more easily fermented than others," p. 279.

"According to Gomberg, all the important properties of triphenylmethyl can be explained on the basis of the following hypothesis: (1) tautomerization of hexaphenyl-ethane to a quinonoid substance having the Jacobson formula; (2) partial dissociation of this compound into positive and negative ions in all solvents; (3) mutual interconvertibility of these ions by tautomeric change; and (4) the existence of the trivalent carbon atoms giving rise to free radicals," p. 303.

"We cannot say definitely that the ethylenic linkage is more or less active than the carbonyl bond; for the matter is influenced in different ways by the reagent employed, the solvent used, and the relative position of the two double bonds in the molecule. In other words, "unsaturation" is not a definite, measurable thing which we can predict in any case from the behaviour of the "unsaturated" substance in other circumstances; it is rather something kinetic, something which is extremely sensitive to external forces, and which in its turn can play a part in influencing the chemical action of groups which it does not apparently affect directly," p. 315.

"In the foregoing sections, no attempts has been made to include all the speculations which have been put forward from time to time with regard to the problem of benzene substitution. Instead, the aim has been to exhibit some of the very different aspects from which the matter can be regarded and in this way to bring out a number of points which stand in more or less close relationship to the main theme. When a problem is still unsolved, it is often quite as important to know what solutions have failed as it is to learn of those which have been partially successful; for in this way the waste of time involved in useless speculations along hopeless roads is avoided by those who wish to reconsider the problem *de novo* for themselves," p. 357.

"There is a second method of reading this history of organic chemistry; for we may take the career of a single investigator and endeavour to trace out how he passed from one line of research to another, and in this way try to put ourselves in his place and see how he was led on logically from problem to problem.

"As an illustration of this, the career of van't Hoff may be sketched in its bare outlines. In his student days, he evolved the idea of stereochemistry and extended the then existing structural chemistry into three dimensions. His next step is seen in his *Ansichten über die organische Chemie* where, amid the discussion of chemical structures, the idea of reaction velocities made its appearance. Three years later, this found a fuller expression in his *Etudes de dynamique chimique*; and the experimental work which was carried out by him in this field brought him face to face with the problem of chemical affinity. Here the affinity which unites the components of double salts attracted his attention and led to his discovery of transition temperatures. A second line of thought from the same starting-point brought him to consider the wider problem of solution and led to his enunciation of the osmotic pressure theory. And in his final completed research he again set out from this same jumping-off ground in order to elucidate the intricate problem of the oceanic salt deposits. From this it is easy to see that van't Hoff proceeded logically from one line of research to its successor; and that his ideas were all of that big and simple type which bear the mark of genius at work.

"Another example of the same kind may be drawn from part of Fischer's career. In an earlier chapter it has been shown how he developed the methods of synthesis in the field of the polypeptides, using the amino-group of one amino-acid to form an amide with the carboxyl group of another amino-acid molecule. At the conclusion of his investigation of the polypeptides he was led to examine a parallel series of reactions: the esterification of a hydroxyl-acid with the hydroxyl group of a second hydroxy-acid. In this way he came into the field of the depsides; and so he was led to approach the moss acids and tannin from the synthetic side. Thus the examination of one series of reactions drew him forward into fresh field, and this, in its turn, opened out into a completely new region of the subject," p. 365.

"The second volume is intended for Honours students and post-graduate workers. It contains a description of the latest work in several fields of interest in modern organic chemistry. In some of these the main work of clearing up the subject has been completed, whilst in others the problems are still unsolved, and all that could be done was to give some account of the present-day position," p. vi. The chapters are entitled: organic chemistry in the twentieth century; some carbohydrate constitutions; the sesquiterpene group; rubber; recent work on the alkaloids; the anthocyanins; the chlorophyll problem; the depsides; some theories of the natural syntheses of vital products; new organo-alkali compounds; other cases of abnormal valency; structural formulæ and their failings; some applications of electronics to organic chemistry; some unsolved problems.

In the form in which it exists to-day, organic chemistry may be said to take its root in the work of Frankland at the middle of last century. Once the doctrine of the constancy of valency was accepted, the way was open for Couper and Kekulé to bring order into the vast mass of material which had been accumulated in earlier times; while, later, van't Hoff and LeBel carried the ideas of molecular arrangement out of two dimensions into three and laid the foundation of our present views. Following in the track of these pioneers, the chemists of the latter half of the nineteenth century rapidly developed the theoretical side of the subject; while, on the other hand, the modern formulæ lent to synthetical work a certainty which had previously been unknown," p. 1.

"On the theoretical side of organic chemistry, to which we must now turn, Thiele's views on valency exerted a considerable influence during the century. It is very seldom that any theory is accepted immediately after being published; usually a considerable time is required during which the chemical world assimilates the author's views in a more or less unconscious manner, until some day they find their way into text-books. It is a remarkable tribute to the value of Thiele's partial valency theory that it became a classic almost as soon as it was published," p. 9.

"The most striking example of intramolecular change is the discovery by Hantzsch of a new class of electrolytes which have been named pseudo-acids and pseudo-bases. Previous to his work, the electrolytes known to us might be grouped under the four following heads: (1) Acids, which give rise to hydrogen ions; (2) Bases, which yield hydroxyl ions; (3) Salts, which dissociate into acidic and basic ions; and (4) Amphoteric electrolytes, which are capable of producing either hydrogen or hydroxyl ions according to the experimental conditions employed.

"Now when an acid solution is neutralized by means of a base, the solution is acidic at the beginning and remains acidic all through the titration until the neutralization-point is reached. On the other hand, if we start with a solution of nitromethane, it is neutral in reaction; and yet if we slowly add to it a solution of sodium hydroxide, the solution does not become alkaline at once. In fact, we may have to add a considerable quantity of alkali before the next drop produces an alkaline reaction in the liquid. Clearly nitromethane is a neutral substance which, *given time*, can exhibit acidic properties in presence of alkali. It is this *slow neutralization* which distinguishes it from a true acid," p. 10.

On p. 11 the author says that "the discovery of the pseudo-acids resulted in the collapse of Ostwald's hypothesis as to the nature of indicators." If the author had substituted the word "broadening" for the word "collapse," his statement would have been true. Ostwald said originally that an acid indicator is a weak acid whose ion has a different color from the undissociated acid. We now say that an acid indicator is a weak acid in which the ion or a product derived reversibly from it has a different color from the undissociated acid or a product derived reversibly from it. That change of wording may mean collapse to an organic chemist; but most chemists have sturdier constitutions.

"In the whole field of stereochemistry, no more puzzling phenomena are known than those grouped under the head of the Walden Inversion; and at the present day we still await a solution of the problem. The data are so complicated that it could be impossible to deal with them fully here: all that can be done is to indicate the nature of the question," p. 16.

"We now come to a subject which lies in the borderland between organic and physical chemistry, namely the relations between the physical properties of compounds and their chemical structure. The problems comprised in this branch have for the most part, been solved by organic chemists, owing to the fact that the material of experiment is largely drawn from the carbon compounds. The curious step-motherly fashion in which this important subject has been treated by the ordinary physical chemist is possibly due to the influence of Ostwald who had a large following among the older group of physical chemists; or it may be ascribed to the fact that few physical chemists have any claim to be ranked as even moderate organic chemists, a fact which handicaps them in this particular line of research. Whatever be the reason, there is no doubt that the relations between chemical constitution and physical properties so fully recognized by van't Hoff, have not been pursued with either eagerness or success by the physical chemists of the Ostwald School," p. 22.

"It is well known to every chemist that when dextro-rotatory cane-sugar (sucrose) is hydrolysed with dilute acids, the resulting mixture of glucose and fructose is laevo-rotatory, whence is derived the term "inversion" to describe the process. The origin of the change in rotatory power is found in the fact that the dextro-rotatory sucrose molecule is split up into a dextro-rotatory glucose molecule and a laevo-rotatory fructose molecule of much higher rotatory power. The result of this is that the mixture possesses laevo-rotation. Now when sucrose is methylated and hydrolysed, the octamethyl-sucrose splits up into tetramethyl-glucose and tetramethyl-fructose; but *no inversion of the sign of the rotatory power is observed*. This apparent anomaly is due to the fact that the methylated fructose residue differs from ordinary fructose in being strongly dextro-rotatory instead of showing laevo-rotation. This furnishes conclusive proof that the fructose molecule is capable of existing in two different forms. As combined in the sucrose molecule, it is in the γ -form; and during the inversion of sugar it reverts to the normal stable fructose type. If this intramolecular rearrangement is prevented by methylation, which lacks the molecular structure, then the product of inversion is the tetramethyl-derivative of the γ -form and not a

derivative of the normal form. This conception of the matter is reinforced by the fact that tetramethyl fructose derived from the methylation of methyl-fructoside differs greatly in physical and chemical character from the tetramethyl-fructose obtained from octamethyl-sucrose. The former compound is stable towards permanganate, the sucrose product is unstable in presence of permanganate; and the two substances present the contrast in rotatory power which was referred to above," p. 46.

"In actual practice, the hydrolysis of cellulose is hemmed in by difficulties. From time to time accounts have appeared in the literature describing how practically quantitative yields of glucose have thus been obtained; but these have been adversely criticized by Irvine and Soutar. These two investigators carried out careful investigations in which only actually isolated glucose was taken into account; and they were able to prove that the glucose yield from cellulose on this basis was a minimum of 85 per cent., which compares very favourably with the normal yields of reactions in the sugar group, since these rarely reach 80 per cent. Later, Monier-Williams recorded a yield of 90.67 per cent. of the theoretical quantity, his result also being based on actually-isolated glucose. Finally, Irvine and Hirst obtained an over-all yield of hexose from cellulose amounting to no less than 95.1 per cent. of the theory. From these figures it seems not unwarranted to suppose that cotton cellulose is essentially composed of glucose units," p. 70.

"The Röntgen diagrams of cellulose hydrate, oxycellulose (derived from oxidation of viscose), and hydrocellulose (prepared by the reduction of viscose), have been found identical with the diagram for lichenin, which shows that all these materials have the same crystalline constituents. This evidence suggests that cellulose and lichenin are both built up from basal units which have the character of glucose anhydrides," p. 75.

Zingiberene sounds like an Edward Lear word; but it seems to be a sesquiterpene found in ginger oil, p. 103. The author says, p. 117, that "this work of Tilden's should be regarded as a real synthesis of rubber, and stands in a different category from Bouchardat's. Bouchardat obtained his isoprene by distilling rubber; so that his work consisted of *re-synthesising* rubber from its decomposition products. Tilden, on the other hand, obtained his isoprene from turpentine, and may thus claim to have made a true synthesis of rubber." This seems very far-fetched. Both men condensed isoprene to a rubber. The source of the isoprene would be a very important matter if this were a commercial problem; but it is quite immaterial so far as the scientific side of the question is concerned. There was no reason to suppose that the source of the isoprene affected its reaction seriously. It is so easy to carry partisanship too far.

The author does not accept the view of Harries, p. 119, that isoprene rubber is dimethyl octadiene.

"Ostromisslenski differed from Harries with regard to the classification of the rubber-like materials produced by synthetic methods. In his view, the physical properties of the product are better indices of its nature than the results of decomposition reactions have proved to be. For example, a determination may be made of the temperatures at which an artificial rubber acquires and loses its elastic properties; and if these temperatures agree approximately with those for natural rubber, Ostromisslenski considered that the synthetic substance is "normal." If, on the other hand, there is little agreement here and if the range of temperature over which the artificial product remains elastic is different from the range found for natural rubber, then the artificial product should be regarded as abnormal," p. 129.

"The isomerism of codeine and pseudocodeine therefore arises from the fact that the $-\text{CH}(\text{OH})$ -group occupies the position 6 in one molecule and the position 8 in the other. These reactions enable us to compare the formulae [for morphine] of Collie and Pschorr. The Collie formula agrees with the facts; whereas in the Pschorr formula the position 8 is already occupied by the isoquinoline ring. From this it is evident that Collie's formula is the more correct of the two," p. 166.

"The solvent chosen for the removal of the pigment from the petals of flowers or the skins of berries varies, of course, according to the nature of the anthocyanin present. In the case of the cornflower, water alone suffices to dissolve the colouring material; hydrochloric

acid in methyl alcohol solution is used in the cases of the rose, the hollyhock, the mallow, the peony, and the bilberry; dilute alcohol is employed to remove the pigments from the larkspur and the scarlet pelargonium; whilst acetic acid is found to be the best solvent in the cases of the grape and whortleberry," p. 174.

"The importance of metallic derivatives of the anthocyanins has been emphasized by some work on the subject. Reduction of a flavone derivative by means of a metal and a mineral acid leads to a production of a red compound; but when magnetism and an organic acid such as acetic acid is employed in presence of mercury, the colour of the product is found to diverge from the normal red tint. . . . The difference between the reaction products when mineral and organic acids are employed has been traced to the fact that the radicle $-Mg.Cl$ is replaced by a chlorine atom if hydrochloric acid is present in quantity; so that the end-product is the red oxonium chloride," p. 186.

"Basing themselves upon these result, Shibata, Shibata and Kasiwagi suggested that metallic complex salts of this type are important factors in flower coloration and give rise to the "blue" anthocyanins. The metallic atoms which they contain are probably calcium and magnesium. The "violet" and "red" pigments are assumed to be complex salts containing fewer hydroxyl groups than the "blue" ones; or to be mixtures of the "blue" compounds with a certain quantity of red oxonium salts which have been formed from the "blue" derivatives by decomposition with acids.

"The existence of these various types would be conditioned by the nature of the sap in the neighborhood of the pigment; and as the sap must obviously be more highly concentrated the nearer we go to the evaporating surface of the petals, it is evident that variations in the structure of the pigment must be expected. Again, the sap in certain parts of the plant may be more alkaline than in others; and as the cyanidins are indicators, it is clear that their tint will be affected by this factor also," p. 187.

"In the higher branches of the vegetable kingdom, chlorophyll plays a most important part in the vital economy of the organism; whilst in animals an equally essential factor is the colouring matter of the blood. The parallel functions of the two compounds suggest that some similarity in nature might be traced between chlorophyll and haemin; and a survey of the chlorophyll problem would be incomplete without a brief reference to the colouring material of blood.

"Examination of the blood pigment shows that it is composed of two portions; an albuminous substance called globin and a non-albuminous compound named haematin. It is with the latter that we are here concerned.

"Both chlorophyll and haematin are metallic derivatives, the magnesium of chlorophyll finding its analogue in the iron of haematin. In each case the metallic atom displays an abnormal character; and both compounds can be freed from their metallic portion by similar treatment. Finally, when analogous degradation methods are employed in the two cases, aetioporporin is produced from both chlorophyll and haematin. These facts are sufficient to justify the assumption that the two substances are related to one another in a more than superficial degree," p. 204.

"Up to the present time the lichens are the solitary abundant natural source of depsides. If Schwendener's views be correct, the lichens are produced by a symbiosis of fungi and algae; and possibly this peculiar origin may account for the presence in their tissues of the depside group, which is so conspicuously scarce in the rest of nature," p. 220.

"How does it come about that the depsides occur so plentifully in one particular type of plant-life? The rarity of the depsides in general, as compared with the profusion of the proteins in nature, can perhaps be accounted for on lines already suggested on an earlier page. Amide-formation depends upon the combination of dissimilar groups, whilst in the esterification of a phenolic acid two groups of a much less unlike character are being linked together. But this serves only to make the case of the natural depsides still more strange; for it is difficult to see why, when they do occur, the plant should produce such relatively enormous yields as are indicated by the high percentage of tannin in galls. Nor does it account for the limitation of the sources of the natural depsides. In this last connection, one point may be suggestive. Every one knows that mosses grow best in dimly-lit localities;

whereas the ordinary plant flourishes only in a good light. Now the normal plant is engaged in building up cellulose, whereas the moss synthesizes a large proportion of depside which is not found in the normal vegetable. Is it beyond the bounds of possibility that there is some connection between these facts; and that photochemical action plays its part in the problem," p. 333?

"All reactions which are likely to be employed in vital syntheses are reversible; and hence if they be carried out in glass test-tubes they must come to an equilibrium point, except in those cases wherein gaseous products are formed. How, then, does the plant succeed in producing its high yields of certain substances which, in a test-tube, would be formed only in minor quantities from the same reagents? When we examine the living plant, we are at once struck by the wonderful mechanism of the natural chemical laboratory which we find there. It is a system of test-tubes made of cellulose and differing from ordinary test-tubes in that the walls are constructed from semi-permeable membranes. Each cellulose test-tube is immersed in a solution differing from that which is contained within the cellulose vessel. The membrane acts not only as a container, as the glass test-tube does, but in addition it behaves as a filter, a concentrator, or a separator. Thus during the progress of a down-grade reaction in which a complex molecule is broken up into constituent parts, the cellulose wall permits a certain product to accumulate in one part of the plant whilst a mixture of other compounds may be withdrawn to a different region. In this way the ordinary equilibrium stage of the reaction is evaded; and much higher yields may thus be attained," p. 237.

"Photochemical effects must, of course, play a very striking part in vital processes, especially in the vegetable kingdom. Of these, the most important from the theoretical standpoint is the discovery by Cotton that the dextro- and laevo- forms of tartaric acid absorb *d*-circularly polarized light to different extents; which implies that such light will decompose them at different rates. Now since light is circularly polarized by the surface of the sea, we have a natural method whereby the production of unequal quantities of asymmetric material can be attained; and once the balance between the two isomers is thus disturbed, the general production of optically active compounds becomes possible. It may be that these experiments indicate the manner in which optically active substances first made their appearance on the earth's surface," p. 246.

"The fatty acids of the acetic series are quite common in nature, whilst their hydroxyl-derivatives—with the exception of lactic acid—are hardly represented at all. Why should this be so? Why do all the important sugars and starches contain a chain of five or six or a multiple of five or six carbon atoms? Why are the majority of the amino-acids obtained from the proteins the α -amino-acids? Why are the ortho- and meta-derivatives so strongly represented among naturally occurring benzene derivatives, whilst the majority of the terpenes are derived from *para*-cymene?

"In the case of such broad generalities there must surely be some simple solution. The curious thing is—not that the answers to these questions are omitted from the ordinary text-books, but rather that the questions do not appear to have suggested themselves to the writers at all," p. 276.

"The abnormal compounds described in the present chapter, as well as their allies among the metal-ketals and the triphenyl-methyl series, cannot fail to suggest problems affecting the very bases of structural chemistry. Once the conception of free radicals is admitted, the long-trying dogma of the quadrivalence of carbon comes into the scales for a final test. It is doubtful if all the older ideas will be suddenly thrown aside. Much more probably we shall simply incorporate the idea of free radicals in our thinking and shall not trouble ourselves too much over the incompleteness of our valency scheme. But the chemistry of free radicals, as it extends, is certain to have a marked influence upon our ultimate conception of valency. During the present generation, there has been a gradual process of facing fresh facts with regard to the chemical bonds, so far as organic chemistry is concerned. This first manifested itself in a preoccupation with residual affinity and partial valencies; then it showed itself in the attempt to bring electronic ideas to bear upon the carbon compounds; and finally, in recent times, the atomic theory of G. N. Lewis seems to

have given us something much more definite and satisfactory than anything which preceded it. It is much too soon, as yet, to consider ourselves on firm ground; but when the further implications of the Lewis theory have been worked out and applied to unsaturated compounds in general, it seems not unlikely that we shall have a much clearer idea of a good many problems than we have at present.

"The case of the free radicals is of special interest from the standpoint of Lewis's theory, since in the triphenylmethyl derivatives carbon acts as an ionogenic element, and thus we have a bridge built between that behaviour of the normal non-ionogenic carbon derivatives on the one hand and the ionisable molecules of salts upon the other hand. Lewis's theory, with its conclusive sweep, seems to offer most interesting possibilities in this region of chemistry," p. 317.

"Intramolecular change furnishes one of the most interesting fields for speculation in organic chemistry. Two problems are evidently involved in the question: for we may inquire, in the first place, why one particular structure is more stable than an isomeric form; or, secondly, we may endeavour to conjecture the mechanism of the process whereby the one isomer is converted into the other. Let us take certain well-known examples of intramolecular changes and see if they can be accounted for by any general principle. It will be sufficient if we examine the pinacone change, the Beckmann rearrangement, the benzylic acid change, and the hydrobenzoin change," p. 359.

The author has a real talent for this sort of thing and it is to be hoped that he will write many more books. There are not many people who can do it and the talents of the few should not be wasted.

Wilder D. Bancroft

A Text-Book of Inorganic Chemistry. Vol. VII, Part I. Edited by J. N. Friend and D. F. Twiss. 23 X 16 cm; pp. xxvii + 370. London and Philadelphia: Charles Griffin and Company, J. B. Lippincott Company, 1924. Price: \$7.50. This part of the volume deals with oxygen. The chapters are entitled: general characteristics of the elements of Group VI; oxygen; the physical properties of oxygen; the chemical properties of oxygen; ozone; the atmosphere; water; physical properties of water; chemical properties of water; composition and molecular complexity of water; water as a solvent—water analysis; hydrogen peroxide.

"The commercial commodity known as "oxylithe" has the following composition: sodium peroxide, 98.32; oxide of iron, 1.00; copper sulphate, 0.68," p. 17.

"The most probable explanation is that alternately higher and lower oxides of manganese are formed—the higher oxide by the oxidising action of the heated chlorate, and the lower oxide by the decomposition of the higher, either alone or in contact with a further supply of chlorate. Mention has already been made of the fact that, when potassium chlorate is heated alone, some perchlorate is formed through self-oxidation simultaneously with the evolution of oxygen. This reaction does not occur in the presence of manganese dioxide, since this oxide effects the decomposition of the chlorate into chloride and oxygen at a temperature considerably below that at which autoxidation of the chlorate proceeds at an appreciable rate," p. 22.

"The theory that the catalyst effects the decomposition [of bleaching powder] by its own alternate oxidation and reduction is supported by the result of passing chlorine into a 50 per cent. solution of sodium hydroxide containing dissolved copper hydroxide; the blue solution at first deposits a yellow copper peroxide, which rapidly decomposes, evolving oxygen and regenerating the original solution. The effect of adding two catalysts to bleaching powder is remarkable. If the bleaching powder is made into a cream with water, oxygen may be liberated at the ordinary temperature by addition of a ferrous or manganese salt and in the presence of a copper or nickel compound. The best result is obtained with a mixture of ferrous and copper sulphates," p. 23.

"Plumboxan, a mixture of the manganate and meta-plumbate of sodium, namely, $\text{Na}_2\text{MnO}_4 \cdot \text{Na}_2\text{PbO}_3$, readily evolves oxygen when heated in a current of steam at 430° to

450° C. The plumbosan is regenerated at the same temperature by replacing the steam with air, the issuing gas, during the initial stages of regeneration, consisting of a fairly pure nitrogen.

"The oxygen obtained by this process is very pure if the precaution is taken to remove the last traces of nitrogen from the pores of the plumbosan after regeneration by connecting to a vacuous vessel before introducing the steam. The chemical reactions taking place are very complex, and but imperfectly understood," p. 26.

When speaking about the assimilation of carbon dioxide by plants under the influence of sunlight, the authors say, p. 27, that "the energy necessary for this reaction, which is endothermic, is obtained from the light, the most active rays being, curiously enough, those of the red, orange, and yellow portions of the spectrum, and not the chemically reactive rays of the blue and violet end." Everybody else considers this as absolutely normal, because the blue and violet rays are not absorbed strongly.

In the production of liquid air by the Claude process, "the difficulty of lubrication appears to have been mainly responsible for the failure of previous attempts, and this was first overcome by the employment of petroleum ether which does not solidify, but merely becomes viscous at such low temperatures as -140° to -160° C. Later, however, it was found that leather retains its ordinary properties at these low temperatures, and in 1912 leather stampings were fitted to the working parts of the machinery to the entire exclusion of lubricants," p. 28.

"Oxygen is also soluble in certain molten metals, *e.g.* platinum and silver, more than twenty times its own volume of the gas being absorbed in the case of the latter metal; the dissolved gas is largely, but not completely, restored at the moment of solidification of the metal, and the phenomenon of "spitting" is thus produced. The power of oxygen to diffuse through heated silver, whereas glass is impervious, is probably due to this solubility of oxygen in the metal," p. 43.

"The rate of oxidation of any particular substance is dependent upon various factors, to wit, its own physical condition as well as that of the oxygen; the presence of moisture or of a catalyser; and the application of light, heat, and pressure. Thus, liquid oxygen does not affect phosphorus or the alkali metals; neither does it combine with solid nitric oxide, although a small jet of burning hydrogen will continue to burn below the surface of liquid oxygen, the water produced being removed as ice and a considerable amount of ozone being formed. Similarly graphite and diamond, when once ignited, will burn on the surface of liquid oxygen, the carbon dioxide produced being frozen and some ozone passing into solution," p. 50.

The author says, p. 52, that "by flame is generally understood a mass of gas raised to incandescence," forgetting that it is practically impossible to heat a transparent gas to incandescence. "It is possible to prepare an active form of oxygen analogous to active nitrogen by subjecting the dry, ozone-free gas to the influence of an electric discharge. It yields a weak, bluish-green afterglow, which is less persistent than that of hydrogen. When mixed with active nitrogen, this active oxygen yields oxides of nitrogen. Both oxygen and ozone are unaffected by active nitrogen. Hence active oxygen is different from these, but is capable of existing for only a short time," p. 52.

After discussing slow oxidation, the authors say, p. 56, that "probably all these theories possess an element of truth; against each of them some objection may be raised; there is yet room for some comprehensive explanation which shall remove all difficulties."

"There has been discovered in the tissues of animals and plants a class of complex organic compounds, termed *ferments* or *enzymes*, which are capable of exerting marked catalytic influence on certain chemical reactions. Some of these substances are catalytically active towards oxidation processes by the atmosphere, and these bodies are frequently distinguished by the term *oxydases*. Oxydases are widely distributed and the discoloration of the freshly broken surface of some fruit is to be referred to atmospheric oxidation induced or aided by an oxydase. Alcoholic tincture of guaiacum resin in the presence of an oxydase undergoes oxidation by free oxygen with formation of a blue coloration, and so provides a convenient reagent for the identification of this type of substance. Manganese, and also

iron, compounds, are frequently present in these oxydases, and it appears probable that in some cases one of these metals, if not both, actually plays an important part in the catalytic process. In some cases, however, compounds of these metals are absent, so that in such oxydases the activating effect appears to be characteristic of the organic enzyme itself," p. 58.

"When a mixture of oxidisable substances is so treated that certain of the constituents only are oxidised to the more or less complete exclusion of the remainder, the process is known as selective oxidation. In cases of gaseous combustible mixtures, the passage over catalyst frequently effects the selective combustion of one constituent. Thus, for example, when a mixture of oxygen, hydrogen, carbon monoxide, methane, and nitrogen is passed over spongy platinum at 177°C. the hydrogen and carbon monoxide are oxidised, but not the methane. This is termed selective oxidation, and is the basis of Hempel's method of analysing certain gaseous mixtures. The selective oxidation of carbon monoxide in excess of hydrogen by passage over catalysts at suitable temperatures has been studied by Rideal, who shows that the oxide of copper (operative at 110°C.) and the oxides of iron and chromium (operative at 250° to 350°C.) are active in inducing the oxidation of the monoxide, although in no case is the selective oxidation complete," p. 59.

"Had Europe possessed an Arctic climate with a maximum temperature below 7°C., it is possible that the discovery of phosphorescence of phosphorus might have been long delayed. Upon ignition with a lighted taper the phosphorescent temperature interval would have been passed so rapidly that the phenomenon would not ordinarily be observed," p. 61.

"It has long been known that certain flames are capable of existence at relatively low temperatures. Thus, a century ago, Davy observed that when a hot platinum wire was introduced into a mixture of ether vapour and air, not only did the wire become red hot in consequence of active surface combustion, but a pale phosphorescent light could be detected above the wire, particularly when the latter ceased to glow, if the experiment were conducted in a dark room. Dosberegner observed the same phenomenon, and mentioned that when ether is dropped into a retort at 100°C. it may assume the spheroidal state accompanied by a pale blue flame, visible only in the dark, and too cool to set fire to other bodies. Perkin suggests several ways by which this phenomenon may be exhibited at lectures. Of these, perhaps the best is to heat an iron or copper ball to dull redness, allow it to cool to such a temperature that it is just invisible in the dark, and, by means of a wire, suspend it over a dish containing several filter papers saturated with ether. As the ball approaches the ether, a beautiful blue flame will form, passing over its heated surface upwards for several inches. The ball may be let right down into the ether without causing ordinary combustion. The blue flame is characterised by its low temperature. The fingers may be placed in it without discomfort; paper is not charred by it, and even carbon disulphide is not ignited by it," p. 76.

"In 1815 Davy suggested that the luminosity of a candle flame is due to the presence of minute particles of carbon at white heat. These particles were believed to be produced by incomplete combustion of the hydrocarbon vapours in the restricted supplies of air available within the flame, the hydrogen of the vapours being "preferentially" oxidized, leaving the carbon to shift for itself. This theory was generally accepted for many years, and it was not until 1867 that a rival theory was projected by Frankland, according to which the luminosity of the flame is due to radiations from dense but transparent hydrocarbon vapours," p. 78.

"From the foregoing it will be evident that a decision between the theories of Davy and Frankland cannot be easily arrived at. Indeed, it is by no means impossible that both theories are correct in so far as they go. The only really certain feature is that the luminous zone is diphasic," p. 79. This is rather hopeless because an oxyhydrogen flame, for instance, is not diphasic. What the authors have overlooked is that there are two independent sources of luminosity in a flame, the incandescence of solid particles, which is a thermal luminescence, and a true chemiluminescence. The problem is quite simple if it is once formulated properly. Davy was right for thermal luminescence; but his view-point does not account for the colors of salt flames. It is not true to say, as the authors do on p. 81

that "the higher the temperature of a flame, the greater will become its luminosity, the change being due to a general shortening of the wave-length of the radiation." This is true only for the case of thermal luminescence.

"By lowering the temperature it is possible greatly to increase the yield of ozone which, under ordinary conditions, is less than 10 per cent. of the oxygen. By immersing an ozonising apparatus in a cooling mixture of ether and solid carbon dioxide and so working at -78°C ., a yield of 11 per cent. has been obtained, whereas in liquid air it was found possible to convert 99 per cent. of the oxygen into ozone, the best results being obtained at this temperature with a pressure of 100 mm., the ozone liquefying out as it is formed," p. 141.

"Obtained in this way, ozone may be purified by fractional distillation at low temperatures, the boiling-point of ozone being some 63° above that of oxygen. The ozonized oxygen liquefied by cooling in liquid air. The deep-blue liquid thus obtained evolves mainly oxygen under reduced pressure and at a certain composition separates into two layers. The upper, dark-blue layer consists of a solution of ozone in liquid oxygen; the lower deep violet-black layer is a solution of oxygen in ozone and contains, at -183°C ., some 30 per cent. of oxygen. All but mere traces of oxygen are removed in a single fractionation of this liquid, and by careful manipulation pure ozone, B.P. -112.4°C ., may be obtained," p. 142.

"Carbon tetrachloride dissolves approximately seven times as much ozone as does water, and when oxygen containing six percent of ozone is passed through the former solvent a distinctly blue solution is easily obtained," p. 146.

"When ordinary ozone is allowed to react with unsaturated organic compounds, the element is sometimes taken up by the latter in groups of four atoms instead of the usual triatomic groups, whereas if the ozone is previously washed by passage through sodium hydroxide solution and sulphuric acid, the addition occurs only by groups of three oxygen atoms. The formation of oxozonides, as Harries terms the products containing O_4 groups, is attributed by Harries to the presence of oxozone O_4 in the crude ozone. The evidence as to the possible existence of a tetratomic form of oxygen, however, cannot yet be considered as satisfactory. Vapour density determinations reveal no tendency on the part of even pure ozone to associate to higher complexes than that corresponding to O_3 ," p. 152. Recent determinations of the vapor density of pure ozone confirm the value 48 for the molecular weight. No tendency to associate to higher molecules has been observed either in the pure liquid or that gas," p. 155.

"As a general rule any harmful effect produced on man by air must be due to some foreign impurity in the air; the mixture of nitrogen and oxygen is an absolute necessity for prolonged existence. The fat of mammals, however, dissolves more than five times as much nitrogen as does an equal amount of water, and this fact may give rise to serious results with men working under conditions, for example, in caissons, in which the external atmospheric pressure undergoes sudden and considerable variations. If the reduction in pressure is too sudden the fat-containing tissues of the workers are liable to injury on account of the formation of gas bubbles," p. 159.

"Not merely does the proportion of oxygen [in the atmosphere] vary from place to place; but it also varies at one and the same place from time to time. Thus Levy found that the air of New Granada underwent remarkable changes, after great forest conflagrations, the oxygen content falling from 21.01 to 20.33 percent. Such a variation is decidedly abnormal, but in volcanic districts is perhaps more frequent than is generally known," p. 163.

"Considerable variation [in the amount of carbon dioxide] may be due to local circumstances. Thus Reiset found that the presence of a flock of 300 sheep on a fine, calm day in Dieppe induced a notable rise in the proportion of carbon dioxide in the immediate neighborhood, which registered 3.18 parts per 10,000 instead of 2.96—the normal value for Dieppe. The influence of vegetation upon the carbon dioxide content of the air has not received the consideration it deserves, although a few isolated experiments have been carried out. Ebermayer, for example, found an excess of the gas in the forest, a result that confirmed the earlier observations of Truchot. In confined spaces, such as dwellings, the carbon dioxide shows a marked increase owing to its being a product of human metabolism, and may reach 0.5 per cent," p. 167.

"From the point of view of ventilation, ozone and peroxides are of interest as they impart a crispness or freshness to the air, and the fact that they are readily decomposed by heat is probably one of the causes of the "flatness" of heated air. The well-known Sanitas preparations are essentially solutions of hydrogen peroxide and of different organic peroxides. There can be no doubt that in nature the presence of hydrogen peroxide is an important factor in removing foetid and putrid matter from the atmosphere. Bosisto has calculated that 96,877,440,000 gallons of eucalyptus oil are held continually at one and the same moment in the leaves of trees massed together and occupying a belt of country over which the hot winds blow in New South Wales and South Australia alone. Kingzett concludes that this amount of eucalyptus oil can and must produce in the atmosphere surrounding the forests no less than 92,785,023 tons of peroxide of hydrogen, and about 507,587,945 tons of the soluble camphor, not to mention the other products of oxidation," p. 177.

"It is interesting to recall the experiments of Lehmann and his colleagues who demonstrated quite recently that when a dust-laden air is breathed through the nose, approximately 40 per cent. of the dust remains in the system, either in the lungs or stomach, the remaining 60 per cent being either respired or retained by the nose and mouth. If, however, the subject breathes through the mouth some 80 per cent is retained by the body. This illustrates the importance of breathing through the nose, but it also illustrates the necessity of reducing the dust in the atmosphere of public rooms and dwellings to the smallest possible amount, as no matter how careful a subject is, some of the dust finds its way into the system," p. 184.

"The presence of moisture in air has a two-fold action upon respiration. First, there is the very obvious fact that if warm air saturated with moisture enters the lungs, the latter will have great difficulty in discharging their superfluous moisture, and a sense of oppression must result. This explains the heavy feeling produced upon entering hot-houses, in which the air, apart from its moisture content, is perfectly good, and very free from carbon dioxide. Cold air, even if saturated with moisture, will not have anything like the same effect, for upon entering the lungs the temperature rises proportionately higher, and the air is thus able to take up much more moisture before becoming saturated, thereby allowing the lungs full opportunity to relieve themselves. Secondly, air containing moisture cannot take up carbon dioxide from the blood as easily as dried air, consequently the ventilation of the lungs is retarded by inhaling moist air.

"These two factors working together are sufficient to show that respired air, being saturated with moisture at a warm temperature, cannot be wholesome, and L. E. Hill and his co-workers regard the moisture content as the main cause of the discomfort of ill-ventilated buildings," p. 186.

"Spring water, particularly that derived from deep-seated springs, is usually beautifully clear and sparkling. The clearness is mainly due to thorough filtering during percolation through the soil, whilst the sparkle is caused by the presence of gases, mainly carbon dioxide, in solution," p. 206. Waters containing hydrogen sulphide "have been used frequently in by-gone days for secret correspondence. Letters written with a solution of lead acetate become legible when dipped, for example, in Harrogate water," p. 209.

"Ferruginous water are bitter to the taste, even one part of iron per million of water being perceptible to the average individual. Such waters, which are widely distributed in Germany and the Netherlands, in America, and elsewhere, are particularly favourable to the growth of minute organisms, such, for example, as the *Crenothrix*, the vitality of which appears to be connected with the secretion of iron within the tissue of its cell walls. This organism flourishes in waters containing 0.3 parts of iron per million of water, and may lead to serious choking of water-mains. Aeration and treatment with lime or with colloidal substances have been adopted with more or less success. Thus, for example, at Amsterdam, intense aeration followed by filtration has reduced the iron content of its water supply from 0.8 parts per million to nil. Iron may also be completely removed from water by passage through a manganese permutit filter," p. 234.

"A very striking instance of the value of sand filtration was afforded by the outbreak of cholera in Hamburg in 1892. The city drew its water from the Elbe and used it in its raw

condition for domestic purposes. No fewer than 1250 per 100,000 of the population perished through cholera. The contiguous town of Altona lost but 221 per 100,000 despite the fact that it drew its domestic water from the Elbe *below* Hamburg, after it had received the sewage pollution from the latter city. This relative immunity was due to the fact that the Altona authorities purified their water by passage through sand filters," p. 235.

"Although the compressibilities of natural waters are exceedingly small, their effect upon the distribution of land and water on the crust of the earth is important. It has been calculated that, in consequence of the compressibility of sea-water, the mean sea-level is 116 feet lower than it would be if water were absolutely incompressible, with the result that two million square miles of land are now uncovered which would otherwise be submerged," p. 264.

"It is interesting to note that whereas ice produced with a cooling temperature within one or two degrees of the melting-point is usually clear, the product obtained with stronger cooling is milky in appearance on account of the inclusion of minute bubbles of air which was previously in solution."

"Livingston mentions that the temperature of the surface water of ponds in the central regions of Southern Africa may reach as high as 38°C., but, owing to the poor conductivity of heat, deliciously cool water may be obtained by anyone walking into the middle and lifting up the water from the bottom," p. 270.

On p. 345 the authors say that "it is interesting to note that, whilst solutions of aniline green and of magenta are not bleached by dilute hydrogen peroxide solution in the dark, yet upon exposure to the light of a quartz-mercury lamp the colours fade readily. It would appear, therefore, that, under the influence of the light, the peroxide becomes increasingly active." While this conclusion may be right it is not necessary. The dye may have been activated by the light.

Wilder D. Bancroft

Erratum

A number of errors have occurred in the proof-reading of the article by Messrs. Swan and Urquhart entitled "Adsorption Equations" (31, 251). The references to Williams under "The Isobar: Theoretical" on pp. 251, 267 should be deleted. In the papers of Williams there referred to, no equation is given for the isobar nor is any derivable from his isostere equation. On p. 253 change the equation at the bottom of the page to $\log \lambda_t = \log \lambda_0 - \theta \log (a/v)$.

On p. 254 change to $(a/v)_\theta = (a/v)_0 - \zeta^\theta$.

On p. 256 change to $\mu = p/\sqrt{2\pi MRT}$

On p. 257 change to $\eta = (N_0/2N)\sqrt{k/m}$, to $\eta \propto p^{1/2}$, and to $C = 2k_2(6k_3k_1 - 2k_3k_4 + k_1k_2 - k_1k_3 - 4k_4^2)$.

On p. 258 change to $X = \int_0^\infty OC_\infty (e^{-E_h/RT} - 1) dh$.

On p. 259 change to $X = \frac{O\delta C_\infty e^{k/T}}{2\mu (k/T)^2}$

On p. 263 change to $\frac{d \log \lambda}{d \log c} = \frac{d \log x}{d \log c} - \frac{1}{\log c_0/c} + \frac{c/c_0}{1 - c/c_0}$

On p. 264 change to curve 2, Fig. 2.

On p. 267 change to $\log x_\theta = \log x_0 - (\zeta - \xi \log p) \theta$, to $\zeta = -dk_\theta/k_\theta d\theta$, and to $\log p_\theta = \log p_0 - \xi \theta$.

On p. 269 change to $y = A\alpha^t \pm B$, $y = A\alpha^t$, or $y = A\alpha^t \pm B\beta^t$, and to "α and β are constants."

On p. 270 change to $k = \frac{1}{t(a - x_\infty)} \left(\log \frac{a - x}{x_\infty - x} \cdot \frac{x_\infty}{a} \right)$

On p. 271 change to dx_t/dt .

On p. 275 change reference 55 to Langmuir: J. Am. Chem. Soc., 38, 2221 (1916).

35-73

STUDIES IN DYEING

BY ROBERT C. HOUCK

SILKS AND DYESTUFFS

Introduction

In dyeing silk with colors not necessarily fast to light and washing, both acid and basic dyes are used. The basic colors are especially adapted to silk because of the clear brilliant tones of pure colors obtained with them. In both cases, dyeing is carried out in a boiled-off liquor bath. The action of the boiled-off liquor or bast soap on the process of dyeing and the effect of addition agents are studied in this thesis.

In black silk dyeing the various coal-tar black dyes have generally a slaty faded appearance. This is due to the fibre being so translucent that the full black color is diluted with an excess of transmitted light. To obtain a good black on silk the fibre must be rendered opaque. Logwood accomplishes this purpose and is used in connection with a tannin mordant. A study is made of the adsorption of tannin by silk in view of this.

In consequence of the unexpected behavior of tannin with silk at different temperatures, it was thought desirable to make a few experiments on the precipitation of tannin by acids, especially in view of the work of Thomas on the precipitation of tannin extracts. It was thought possible that a pure tannin might precipitate pretty sharply at a given degree of acidity; but this proved not to be the case.

Addition Agents in the Dyeing of Silk with Acid and Basic Dyes

Numerous theories have been formulated to explain the process of dyeing. Briggs and Bull¹ have shown conclusively that in the dyeing of wool the taking up of acid and basic dyes is a case of adsorption.

The adsorption theory has been summarized at length by Bancroft.² With acid dyes the theory is as follows. In the presence of a solution a fibre tends to adsorb everything in the solution varying with the nature, concentration, and temperature of the solution and with the nature of the fibre itself. With an acid dye in acid solution the constituents of the dye-bath would be hydrogen ions, sodium ions if the dye were a sodium salt, dye anions, acid anions, and undissociated compounds. The hydrogen ions being more strongly adsorbed as a rule than any of the other univalent cations present, and the dye anions being adsorbed more strongly for the same concentration than the other anions, the free dye acid is what is adsorbed normally.³ The dye anions have to compete with the other anions and therefore the addition of strongly

¹ J. Phys. Chem., 26, 845 (1922).

² J. Phys. Chem., 18, 1, 18, 385 (1914); 19, 50, 145 (1915).

³ Bancroft: J. Phys. Chem., 18, 10 (1914); "Applied Colloid Chemistry," 115 (1921).

adsorbed anions will cut down the amount of dye taken up by the fibre while the addition of strongly adsorbed cations will increase the amount of dye taken up. A high concentration of hydrogen ions will therefore increase the adsorption of acid radicals. This means that acid dyes will be taken up most readily in acid solution; but that they may be taken up in neutral or alkaline solution. Sulphuric acid will cause less of an acid dye to be taken up than an addition of an equivalent amount of hydrochloric acid or than the addition of isohydric hydrochloric acid. The addition of sodium sulphate to the bath will cut down the adsorption of an acid dye and will cause more even dyeing.

The effect of the addition of any definite reagent¹ to the dye-bath may be the result of several factors. It may affect either the fibre or the dye-bath. The reagent added may either act chemically on the fibre or be adsorbed and in so doing change the adsorption of the other substances present in the bath.

With the dye-bath the effect may be more complicated. The reagent may react chemically with the dye as in the case of Crystal Violet and potassium hydroxide, giving in this instance a white insoluble leuco base. If the dye is in true solution it might change the solubility of the dye and thus change the amount adsorbed. If the dye is in colloidal solution it might affect the degree of dispersion and alter the amount taken up. The reagent may also change the hydrogen ion concentration. This factor has been shown to be of great importance by Pelet-Jolivet² and by Briggs and Bull³ who studied it quantitatively.

The adsorption theory has been shown by Briggs and Bull to apply strictly to the dyeing of wool with acid dyes. They showed that that acid dyes are taken up by wool best from acid solution and that the amount taken up increases with the hydrogen ion concentration. They also showed that addition agents, as sodium sulphate, change the amount adsorbed, and in this instance that the sodium sulphate decreases the adsorption as demanded by the theory. The theory should apply to the dyeing of silk in the same way and this will be shown later in this paper.

Basic Dyes and the Adsorption Theory

With basic dyes the theory is stated as follows. "A basic dye is taken up most readily in an alkaline solution but may be taken up in a neutral or acid solution. This follows from the fact that in the case of basic dyes the color is in the basic radical of the dye, the dye dissociating in aqueous solution giving colored cations. Hence if the dye is present in an alkaline dye-bath the hydroxyl ions, being as a rule adsorbed more than any other univalent anion present, promote the adsorption of the full color base of cations. The presence of cations in the bath other than those of the dye will cause the amount of a basic dye taken up by the fibre to be cut down. In the same way readily adsorbed anions will increase the adsorption of the dye. Addition of sulphuric acid to the dye-bath will cause more of a basic dye to be adsorbed than

¹ J. Phys. Chem., 26, 846 (1922).

² Chem. Abs., 2, 2159 (1908).

³ J. Phys. Chem., 26, 845 (1922).

an equivalent amount of hydrochloric acid or than the addition of isohydric hydrochloric acid. The addition of sodium sulphate will increase the amount of basic dye taken up by the fibre."

Briggs and Bull have studied the dyeing of wool with basic dyes and have shown it to be an adsorption phenomenon. The theory being correct should hold for silk in the same manner as for wool. This will be shown to be the case later in this paper.

Although basic dyes are not very fast to light and washing, they are used extensively with silk because they give colors of great brilliancy with this fibre. Moreover the requirements of fastness to light and washing are not so strict, as a rule, for silk. Hübner¹ says that the dyeing of silk is strictly a physical or mechanical operation. Pelet-Jolivet² shows that in dyeing silk with a basic dye, methylene blue, the amount of dye taken up is a maximum in alkaline solution, and a minimum in acid solution. Data obtained by them are given in Table I.

TABLE I

Adsorption of Methylene Blue by Silk

Volume of dye bath 50 cc.

Concentration of Methylene Blue = 0.8%.

Weight of silk = 0.3 g.

| Fibre | 2 cc. N/10 HCl | Methylene Blue adsorbed, mg | |
|-------|----------------|-----------------------------|----------------|
| | | Neutral Solution | 2 cc. N/10 KOH |
| Silk | 1.3 | 10.8 | 40.6 |

This is as it should be for, according to the theory, basic dyes should be taken up best from alkaline solution. Both Briggs and Bull and Pelet-Jolivet give data showing how the adsorption of basic dyes by wool varies with increasing alkalinity in the first case and with increasing acidity in the second case. This checks the theory. Only the above data for silk are available. Results similar to those for wool should be obtained for silk. The variation in the adsorption of basic dyes by silk in acid solution will be shown later.

Pelet-Jolivet³ in studying the effect of addition agents in the dye-bath found that 0.5 grams of silk in 50 cc. of 0.2 percent methylene blue solution took up 18.4 mg. dye with sodium sulphate in the bath and 10.8 mg. when alone. These data point to the theory being correct when applied to the dyeing of silk.

However, H. Salvaterra⁴ made a quantitative study on the dyeing of silk with basic dyes, dyeing the silk with a series of closely related dyes. He found from his experiments that the amount of color taken up varied in the same manner as the molecular weights of the color bases. He concluded from these experiments that the dyeing was a chemical process and supported the theory

¹ J. Chem. Soc. 91, 1057 (1907).

² Pelet-Jolivet: "Die Theorie des Färbeprozesses," 95 (1910).

³ "Die Theorie des Färbeprozesses," 118 (1910).

⁴ J. prakt. Chem. 88, 502 (1913).

of salt formation between the color base and the silk. The data from which he drew these conclusions are given in Table II.

TABLE II
Dyeing of Silk with Basic Dyes

Time of run $1\frac{1}{2}$ hours.
Temperature boiling water bath

| Dyestuff | Material for run Silk | Dye | Found on 1 g. silk | Mol. Wt. of dye | (A) Ratio of Mol. Wt. | (B) Ratio of dye on 1 g. silk | Diff. A and B |
|-----------------------|-----------------------------|------|--------------------------|-----------------------|--------------------------------|-------------------------------------------|------------------------|
| p-Fuchsin | 4.79 | 1.21 | 0.022 | 305 | 1.00 | 1.00 | 0.0 |
| Fuchsin | 7.43 | 1.87 | 0.024 | 333 | 0.92 | 0.92 | 0.0 |
| New Fuchsin | 8.78 | 2.23 | 0.026 | 347 | 0.88 | 0.85 | 3.2 |
| Crystal Violet | 6.76 | 1.69 | 0.030 | 389 | 0.78 | 0.74 | 5.7 |
| New Solid Green 3B | 9.39 | 2.36 | 0.032 | 415 | 0.73 | 0.69 | 5.6 |

These results which are the only data given by Salvaterra are hardly sufficient ground on which to base his conclusions. His data given for the amount of dyestuff taken up by one gram of silk must have been calculated from the amount taken up by the different amounts of silk he used with the different dyes. These amounts of dye "taken up by one gram silk" therefore are not comparable and his values as listed are not necessarily what one gram of silk alone would have adsorbed. One thing he should have done to substantiate his theory was to have studied the variation in the concentration of the dye in the bath and the dye in the fibre in a series of experiments with a given dye.¹ "If the dye forms a sparingly soluble compound with the fibre, the fibre and the compound with the fibre would form two separate phases and consequently the composition of the dye in the bath would stay constant as long as any of the fibre compound was forming. Then the concentration of the bath would vary and that of the dye in the fibre would stay constant. In case it was adsorption the concentration of the dye in the bath and in the fibre would vary continuously." Salvaterra also forgot or neglected to consider the work of Sisley² who dyed silk with fuchsine and decolorized it. The operation was repeated several times without the silk losing weight. This³ is a "decisive proof against the assumption that a salt formation had occurred between the dye and the fibre." Another factor which seems to disprove the chemical theory is the work of Freundlich and Losev.⁴ They state that the "partition of a basic coloring matter between carbon or silk, etc., and an aqueous solution follow the same law and that it is adsorption." Silk would

¹ Bancroft: J. Phys. Chem., 18, 2 (1914).

² Bull., 25, 865 (1910).

³ Bancroft: J. Phys. Chem., 18, 135 (1914).

⁴ Z. physik. Chem., 59, 284 (1907).

have to play the part of an acid or a base in this case which might be but it seems impossible for one to have to consider, in the same way, carbon acting as an acid or base.¹

Because of the data of Pelet-Jolivet² pointing to the correctness of the adsorption theory and because no adsorption curves for the dyeing of silk had been made it was deemed necessary to substantiate the adsorption theory as applied to the dyeing of silk. It is found in commercial dyeing of silk that the addition of sodium sulphate to the bath cuts down the amount of dye taken up whether acid or basic. This is a further reason for checking the correctness of the adsorption theory.

The first part of this paper is concerned with showing that the adsorption theory is correct, applying to the dyeing of silk exactly as for wool.

Experimental

The silk used in this work was a first-class grade of degummed silk, obtained through the courtesy of Professor T. B. Johnson of Yale. In some earlier work done on the adsorption of tannic acid by silk, this commercial silk was heated in a ten percent soap bath for one hour at 95°C. This process was repeated using a five percent soap bath to ensure complete degumming. The silk was then washed thoroughly with distilled water to remove the soap and dried. Experiments showed, however, that this was not necessary. The silk as supplied had been degummed as completely as possible, because the silk as supplied and that undergoing the further treatment gave results which agreed closely enough to make it possible to dispense with the soap treatment.

The dyes used were supplied by E. I. duPont de Nemours and Company for the earlier work of Briggs and Bull in their study of the dyeing of wool. The acid dye employed was duPont Orange II and the basic dye duPont Crystal Violet E.

The "bast soap" used in the latter part of the work was made by degumming raw silk, using neutral, powdered sodium oleate, as supplied by Powers-Weightman and Company for the degumming agent. The raw silk was degummed by heating first in a ten percent soap bath for one hour at 95°C and then in a five percent soap bath for the same time and at the same temperature. After using the soap baths for several successive treatments the soap becomes thoroughly charged with the sericin and this liquor was used as the bast soap.

The general procedure throughout the work was to make up a dye-bath of known composition to a total volume of 250 cc. This was then attached to a return condenser to prevent evaporation and heated to the temperature of the boiling water bath, about 95°C. One-gram pieces of silk were placed in the bath at this temperature and kept at this temperature for forty-five minutes. At the end of this time the silk was removed directly from the hot bath. The bath was then allowed to cool down to room temperature.

¹ Bancroft, J. Phys. Chem., 18, 2 (1914).

² Pelet-Jolivet: "Die Theorie des Färbeprozesses" 95, 118 (1910).

The amount of dye taken up by the fibre was determined by difference after the amount left behind in the bath had been determined. The amount left behind in the bath was determined by titration of aliquot portions of the cooled bath with titanium trichloride. The method followed is that suggested by Knecht¹ which had been successfully used later by Salvaterra,² Briggs and Bull,³ and Paddon.⁴ The titanous chloride used was standardized directly in terms of the dye being used by titrating a standard solution of the dye to a colorless solution. During the titration the solution titrated was boiled and air was excluded, being displaced by an atmosphere of hydrogen. Orange II titrates to a colorless endpoint in the presence of an excess of Rochelle salt. Crystal Violet E in the presence of Rochelle salt titrates to a colorless endpoint with the separation of a white precipitate which does not interfere, however, with seeing the endpoint. Sodium bicitrate, quite by accident, was found to work very well in this titration. In the presence of this compound Crystal Violet E titrates to a colorless endpoint without the separation of the white precipitate. The change from Rochelle salt to sodium bicitrate does not affect the result in any way and should not, for Piccard⁵ states that the tartaric acid in Rochelle salts exerts a catalytic action on the action and he recommends the use of one percent hydrofluoric acid which acts similarly. Sodium bicitrate presumably acts in exactly analogous manner.

Determination of the dye left in the bath containing "bast soap" at first presented one difficulty. Titration of an aliquot portion of a dye-bath containing this soap resulted in the use of more of the standard titanous salt than corresponded to that required for the dye when present alone. This difficulty was first met by standardizing the titanous chloride with a standard containing the same percentage of soap as used during a series of runs. This difficulty disappeared when sodium bicitrate was used in the place of the Rochelle salt. Using the bicitrate the volume of titanous chloride checked very closely when titrating a standard containing soap and when titrating a standard with no soap.

Final hydrogen ion concentrations were determined in the case of the experiments with Orange II to see if as in the case of wool the amount of dye taken up varied continuously with the hydrogen ion concentration. The hydrogen electrode was used in these determinations. The electrode vessel employed was the simplified form of the Lewis, Brighton, and Sebastian device.⁶

Hydrogen used for the electrode was electrolytic hydrogen from a tank and before using was passed through alkaline pyrogallol, water and sulphuric acid. Passing the hydrogen through a quartz tube containing a heated nichrome spiral was not resorted to as it has been found not to be necessary.

¹ Knecht: Ber., 36, 1552 (1903); 38, 3322 (1905).

² J. prakt. Chem., 88, 502 (1913).

³ J. Phys. Chem., 26, 845 (1922).

⁴ J. Phys. Chem., 26, 384 (1922).

⁵ Piccard: Ber., 42, 4341 (1919); Knecht: "New Reduction Methods in Volumetric Analysis," 8 (1918).

⁶ J. Am. Chem. Soc., 39, 2250 (1917).

Saturated calomel electrodes were used as the standards and the potentials were measured at room temperature using a Leeds and Northrup precision potentiometer. It is not necessary in work of this type to use an instrument as sensitive as this one since the accuracy of determinations of pH of dye-baths is not exceedingly great.

Silk and Hydrochloric Acid

First a study of the adsorption of an acid by silk was made. Concentration of acid in the bath and of acid in the fibre should vary continuously if the silk shows adsorption of the acid. One gram pieces of silk were heated

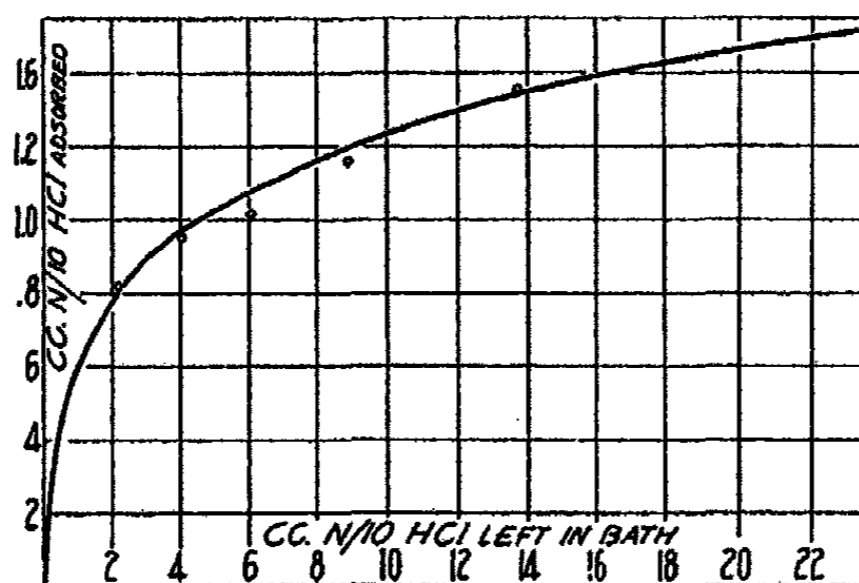


FIG. 1
Adsorption of HCl by Silk

at the temperature of the boiling water bath with dye-baths of known composition and the acid adsorbed determined by difference after the acid left in the bath had been determined. The data for this series of experiments are given in Table III.

TABLE III
Adsorption of HCl by Silk

Weight of silk 1 g.

Volume of bath 250 cc.

Temperature Boiling water bath.

| cc. N/10 HCl at start | cc. N/10 HCl at end | cc. N/10 HCl adsorbed |
|-----------------------|---------------------|-----------------------|
| 1.0 | 0.76 | 0.24 |
| 2.0 | 1.34 | 0.66 |
| 3.0 | 2.18 | 0.82 |
| 5.0 | 4.05 | 0.95 |
| 7.0 | 5.99 | 1.01 |
| 10.0 | 8.84 | 1.16 |
| 15.0 | 13.64 | 1.36 |
| 25.0 | 23.48 | 1.52 |

These data show that the acid concentration in the bath is varying continually, as it should for adsorption. Plotting these data a curve is obtained which shows this very plainly as seen in Fig. 1.

Acid Dyes and Silk

Silk was next dyed with Orange II in acid solution for, according to the theory, acid dyes should be taken up best from acid solution. The silk was entered at the temperature of the boiling water bath and removed at the same temperature. The results of the experiments are given in Table IV.

TABLE IV

| Adsorption of Orange II by Silk | | |
|---------------------------------|--------------------|----------|
| Volume of dye bath | 250 cc. | |
| Weight of silk | 1 g. | |
| Amount of dye | 75 mg. | |
| Temperature | Boiling water bath | |
| Time of run | 45 minutes | |
| cc. N/10 HCl at start | mg. dye adsorbed | Final pH |
| 0.0 | 2.8 | 7.34 |
| 1.0 | 16.4 | 4.17 |
| 2.0 | 27.7 | 3.95 |
| 3.0 | 37.9 | 3.07 |
| 4.0 | 40.35 | 2.72 |
| 8.0 | 43.08 | 2.37 |
| 15.0 | 45.5 | 2.17 |
| 25.0 | 30.0** | 1.70 |
| 50.0 | 47.7 | 1.53 |

**The value for the amount of dye adsorbed in this case is obviously wrong.

From these data it is clearly seen that the amount of dye taken up varies continuously with hydrogen ion concentration. As the hydrogen ion concentration increased, the amount of dye taken up also increased. This is in accord with the theory which formulated an increase in adsorption of acid dyes in acid solution.

Next a study was made of the effect of the addition of sodium sulphate when added to the dye bath. The conditions were kept exactly the same as before except for the addition of the tenth-normal sodium sulphate solution.

TABLE V

| Effect of Sodium Sulphate on Adsorption of Orange II by Silk | | |
|--------------------------------------------------------------|------------------------------------------|------------------|
| Volume of bath | 250 cc. | |
| Weight of silk | 1 g. | |
| Amount of dye | 75 mg. | |
| Temperature | Boiling water bath | |
| Time of run | 45 minutes | |
| cc. N/10 HCl added | cc. N/10 Na ₂ SO ₄ | mg. dye adsorbed |
| 10.0 | 0.0 | 38.67 |
| 10.0 | 25.0 | 27.78 |

These two experiments show that the addition of a strongly adsorbed anion as the sulphate anion cuts down the adsorption of the dye. This is as it should be. No further work was done with the effect of sodium sulphate on the dyeing with acid dyes except later to see the effect played by bast soap in silk dyeing. The reason for not carrying these experiments any farther here was that greater interest centered upon the basic dyes.

From these two sets of experiments one is safe in concluding that the dyeing of silk by acid dyes is an adsorption phenomenon.

Basic Dyes and Silk

Experiments were next made, dyeing silk with basic dyes. The basic dye employed was duPont Crystal Violet E which can easily be determined by titration with titanous chloride in the presence of an excess of either Rochelle salt or sodium bicarbonate.

According to the theory of dyeing, basic dyes should be taken up most from an alkaline solution. An attempt was made to dye silk with Crystal Violet E in alkaline solution. When the silk was added to the hot bath the colorless leuco base was precipitated. However this dye can be used in neutral or slightly acid solution. Commercially it is used in slightly acid solution.

A study was made of the dyeing of silk with Crystal Violet E in acid solution. The first experiments were made with the bath acidified with sulphuric acid. The results are shown in Table V.

TABLE VI
Adsorption of Crystal Violet E by Silk

| | |
|--------------------------------------------------|--------------------|
| Volume of bath | 250 cc. |
| Weight of silk | 1g. |
| Amount of dye | 75 mg. |
| Temperature | Boiling water bath |
| Time of run | 45 minutes |
| | |
| cc. N/10 H ₂ SO ₄ added | mg. dye adsorbed |
| 0.0 | 48.3 |
| 2.0 | 21.5 |
| 5.0 | 9.0 |

These experiments show that more dye is taken up in neutral solution than in acid solution and that the amount taken up in acid solution decreases with increasing acidity. These results agree with the theory.

Since acetic acid is used to a great extent in the dyeing of silk with acid and basic dyes, a study was made with it replacing the sulphuric acid. The results of a set of experiments are shown in Table VII.

TABLE VII

Adsorption of Crystal Violet E by Silk from Baths acidified with Acetic Acid

Volume of bath 250 cc.

Weight of silk 1 g.

Amount of dye 75 mg.

Temperature Boiling water bath

Time of run 45 minutes

| cc. N/10 CH ₃ COOH | mg. dye adsorbed |
|-------------------------------|------------------|
| 0.0 | 48.3 |
| 2.0 | 25.5 |
| 5.0 | 16.3 |

Comparison of these results with those of Table VI shows that more dye is taken up in baths acidified with acetic acid than from baths acidified with an equivalent amount of sulphuric acid. This is as it should be. Two factors play a part in determining this difference. First the difference in the adsorption of the sulphate and acetate ions would lead one to conclude that the adsorption ought to be greater from sulphuric acid baths. This follows from applying the Schulze-Hardy valence rule which would predict a greater adsorption of the sulphate anion than the acetate anion because of the difference in their valences. However the more important factor in this case is the degree of ionization of the two acids. Acetic acid is considered a weak acid while sulphuric acid is relatively a strong acid. At 25°C. a solution of sulphuric acid containing 0.05 mols of acid per liter (tenth normal) is 64.8 percent ionized while a 0.1 molar acetic acid solution (tenth normal) is only 1.3 percent ionized. As a result the adsorption of hydrogen ions by the silk in case of the sulphuric acid baths would be greater and the amount of dye taken up would necessarily be cut down over that for the acetic acid baths. The results shown by Tables VI and VII are in agreement with the theory.

A study was then made of the effect of addition agents on the dyeing of silk with basic dyes, the one studied being sodium sulphate as before.

TABLE VIII

Effect of Addition Agents (Sodium Sulphate) on the Adsorption of Crystal Violet E by Silk

Volume of bath 250 cc.

Weight of silk 1 g.

Amount of dye 75 mg.

Temperature Boiling water bath

Time of run 45 minutes

Bath acidified with sulphuric acid

| cc. N/10 H ₂ SO ₄ | cc. N/10 Na ₂ SO ₄ | mg. dye adsorbed |
|-----------------------------------------|------------------------------------------|------------------|
| 0.0 | 0.0 | 48.3 |
| 2.0 | 0.0 | 21.5 |
| 5.0 | 0.0 | 9.5 |
| 5.0 | 25.0 | 17.5 |

This was repeated using N/10 acetic acid in place of the sulphuric acid. The results of a series of experiments are shown in Table IX.

TABLE IX
Effect of Sodium Sulphate on the Adsorption of Crystal Violet E by Silk in CH₃COOH Baths

| cc. N/10 CH ₃ COOH | cc. N/10 Na ₂ SO ₄ | mg. dye adsorbed |
|-------------------------------|------------------------------------------|------------------|
| 0.0 | 0.0 | 48.3 |
| 2.0 | 0.0 | 25.5 |
| 5.0 | 0.0 | 16.3 |
| 5.0 | 25.0 | 35.5 |

Another series of experiments was run to show that this effect is general and not specific for a given acid concentration. The data are given in Table X.

TABLE X
Effect of Sodium Sulphate on Adsorption of Crystal E by Silk from CH₃COOH Baths

| cc. N/10 CH ₃ COOH | cc. N/10 Na ₂ SO ₄ | mg. dye adsorbed |
|-------------------------------|------------------------------------------|------------------|
| 0.0 | 0.0 | 54.7 |
| 1.0 | 0.0 | 29.1 |
| 1.0 | 25.0 | 36.6 |
| 2.0 | 0.0 | 22.1 |
| 2.0 | 25.0 | 26.67 |
| 3.0 | 0.0 | 17.8 |
| 3.0 | 25.0 | 29.6 |

These results agree very nicely with the theory. The addition of a strongly adsorbed anion as the sulphate ion should increase the adsorption of the dye and this is shown very clearly by the above data.

The results of the work done so far can be summarized by saying that the adsorption theory does apply very satisfactorily to the dyeing of silk when the silk is dyed with either acid or basic dyes. It now remains to be shown why in commercial practice sodium sulphate apparently decreases the amount of an acid or basic dye taken up by silk.

Practical Silk Dyeing

In the practical dyeing of silk there is added to the dye-bath a certain percentage by volume of "bast soap," or "boiled off liquor." Bast soap is the product obtained by the heating of raw silk with hot strong soap solutions. The raw silk fibre is composed essentially of two parts, the outer casing called sericin or silk glue and the inner fibre or fibroin. The reeled silk as it appears in trade consists of 70-75 percent of fibroin and 30-25 percent of sericin or silk glue. The sericin causes the raw fibre to be harsh and rough; containing most of the coloring matter it gives to the raw fibre the straw-colored appearance which is associated with it. The sericin is soluble in hot soap baths and

is easily removed by heating with soap. The soap is used for many treatments and becomes heavily charged with the waxy and glue-like sericin. This heavily sericin-charged soap is called bast soap or boiled-off liquor and is very much used in making up dye-baths for silk dyeing.

The addition of bast soap to the dye-bath is the factor which causes sodium sulphate apparently to cause a decrease in the amount of a basic dye taken up.

The use of bast soap in the art of silk dyeing has long been resorted to. Napier¹ says that Perkins in his original statement stated "that in silk dyeing the principal difficulty is due to the great affinity of the dyes for the fibre which prevents even dyeing. After a time it was found that this could be overcome by dyeing the silk in a weak soap lather. This causes dyeing to proceed less rapidly and keeps the face of the silk in good condition.

Matthews² states that silk is usually dyed with basic dyes in a dye bath containing "boiled-off liquor" broken or neutralized by acetic acid. He also states that ordinary soap can be used in the place of the bast soap or that it may be omitted entirely, the dye-bath being made up with acetic acid alone. Matthews³ gives the following reasons for the use of boiled-off liquor:

1. "The boiled-off liquor acts as a regulator in the dyeing process; retards the adsorption of color and gives more regular and better penetrated dyeings."
2. "Its use prevents loss of weight of the silk especially if there is much silk glue still left on the fibre."
3. "It adds to the softness and lustre of the dyed silk."

Whittaker⁴ says that basic dyes are best applied in a perfectly neutral bath or in a boiled-off bath just neutralized or broken with acid. He says that the acid in the bath keeps the color off the silk and prevents good exhaustion of the dye-bath.

Numerous other references could be given which deal with the dyeing of silk and the author in every case mentions or recommends the use of boiled-off liquor in silk dyeing.

Matthews⁵ states: "though the practice of using bast soap has been carried on for a long time and is almost universal, the absolute necessity of its employment has been questioned. Ganswindt⁶ claims to have shown by practical tests that the results obtained without the boiled-off liquor are equally as good as those obtained otherwise, the lustre, feel of fibre, and other properties being the same. Though the presence of the bast soap retards the velocity of dyeing (aiding the penetration and evenness of the color), it also prevents good exhaustion of the dye-bath which is a draw-back." Matthews, as stated above, says that the boiled-off liquor may be omitted. Springer⁶ says it is not necessary to use boiled-off liquor if the silk is completely degummed

¹ Napier: "Manual of Dyeing," 382 (1875).

² Matthews: "Application of Dyestuffs," 250 (1920).

³ Matthews: "Application of Dyestuffs," 197-199 (1920).

⁴ Whittaker: "Dyeing with Coal Tar Dyes," 16 (1919).

⁵ "Theorie und Praxis der modernen Färberei," II, 16.

⁶ "Dyestuffs," 24, 56 (1923).

It has been shown in this paper that the adsorption theory does apply to the dyeing of silk when dyed in the absence of boiled-off liquor. It remains now to show experimentally that bast soap does cut down the amount of dye taken up and to show why.

Experiments were carried out to show the decrease in adsorption of dyes by silk in the presence of bast soap. The bast soap used was prepared as described at the beginning of this paper. The results with acid dyes are given in Table X.

TABLE X
Adsorption of Orange II by Silk in the Presence of Bast Soap

| Volume of bath 250 cc. | | | |
|--------------------------------|------------------------------------------|---------------|------------------|
| Weight of silk 1 g. | | | |
| Amount of dye 75 mg. | | | |
| Temperature Boiling water bath | | | |
| Time of run 45 minutes | | | |
| cc. N/10 HCl | cc. N/10 Na ₂ SO ₄ | cc. bast soap | mg. dye adsorbed |
| 10.0 | 0.0 | 0.0 | 38.67 |
| 10.0 | 25.0 | 0.0 | 27.78 |
| 10.0 | 25.0 | 25.0 | 6.00 |

These results check commercial practice. Since acid dyes are affected in this manner it would be natural to expect basic dyes to act in the opposite way, namely that bast soap should force the dye on the fibre. Experimental results showed, however, that, just as in the case of acid dyes, the amount of basic dyes adsorbed in the presence of bast soap was decreased materially. Data for Crystal Violet E and Silk are given by Tables XII and XIII.

TABLE XII
Adsorption of Basic Dyes by Silk in the Presence of Bast Soap

| Volume of bath 250 cc. | | | |
|-----------------------------------------|------------------------------------------|---------------|------------------|
| Weight of silk 1 g. | | | |
| Weight of dye 75 mg. | | | |
| Temperature Boiling water bath | | | |
| Time 45 minutes | | | |
| cc. N/10 H ₂ SO ₄ | cc. N/10 Na ₂ SO ₄ | cc. bast soap | mg. dye adsorbed |
| 0.0 | 0.0 | 0.0 | 48.3 |
| 2.0 | 0.0 | 0.0 | 21.5 |
| 5.0 | 0.0 | 0.0 | 9.5 |
| 5.0 | 25.0 | 0.0 | 17.5 |
| 5.0 | 25.0 | 25.0 | 6.1 |

This was repeated replacing the sulphuric acid by acetic acid. The data for these experiments are given in Table XIII.

TABLE XIII

Adsorption of Crystal Violet E by Silk in Presence of Bast Soap

| cc. N/10 CH ₃ COOH | cc. N/10 Na ₂ SO ₄ | cc. bast soap | mg. dye adsorbed |
|-------------------------------|------------------------------------------|---------------|------------------|
| 0.0 | 0.0 | 0.0 | 13.3 |
| 2.0 | 0.0 | 0.0 | 25.5 |
| 5.0 | 0.0 | 0.0 | 16.3 |
| 5.0 | 25.0 | 0.0 | 35.5 |
| 5.0 | 25.0 | 25.0 | 4.5 |
| 45.0 | 25.0 | 25.0 | 2.9 |
| 70.0 | 25.0 | 25.0 | 20.0 |

It is thus shown clearly that the addition of bast soap to the dye-bath cuts down the adsorption of a basic dye by silk. The high result with acetic acid in Table XIII is explained by a decrease in solubility of the dye when a large volume of acetic acid was added to ensure complete neutralization of the bast soap. This result, however, is in accord with the theory for the amount of dye taken up is still less than when bast soap was omitted from the bath.

It was thought that the same result, decrease in adsorption, could be obtained by dyeing first in a bath containing only the soap and secondly repeating but adding sodium sulphate to the bath. A series of experiments were made varying the different substances in the bath. The data obtained are given by Table XIV.

TABLE XIV

Adsorption of Crystal Violet E by Silk reversing the Order of adding Assistants to the Dye bath

Volume of bath 250 cc.
 Weight of silk 1 g.
 Weight of dye 75 mg.
 Temperature Boiling water bath
 Time of run 45 minutes

| cc. N/10 CH ₃ COOH | cc. N/10 Na ₂ SO ₄ | cc. bast soap | mg. dye adsorbed |
|-------------------------------|------------------------------------------|---------------|------------------|
| 0.0 | 0.0 | 0.0 | 52.7 |
| 0.0 | 0.0 | 25.0 | 4.1 |
| 0.0 | 25.0 | 25.0 | 2.9 |
| 5.0 | 0.0 | 25.0 | 4.0 |
| 5.0 | 25.0 | 25.0 | 2.6 |

The results of this series of experiments show that the bast soap in every case causes a decrease in the adsorption of the dye by the fibre.

This can only be explained by saying that in both cases the bast soap as a whole is taken up preferentially by the fibre and as a result the amount of dye adsorbed by the fibre is cut down materially. Another factor which undoubtedly aids in the case of Crystal Violet E is that Crystal Violet is

considered to be partly colloidal.¹ Diffusion experiments indicate this to be the case with Crystal Violet E. This means that the dye may act to some extent as a substantive dye, especially in the presence of a peptizing agent. Some of the bast soap might act as the peptizing agent and in this way cut down the adsorption to a certain extent. This has been shown to be the case with substantive dyes by Briggs.²

Summary

1. A study has been made of the adsorption theory of dyeing, applying it to the dyeing of silk with acid and basic dyes.
2. The dyeing of silk has been found to be an adsorption phenomenon and follows the adsorption theory conclusively.
3. The action of assistants has been studied, in particular the action of sodium sulphate and bast soap. The action of sodium sulphate checks the theory.
4. The results obtained in practice which apparently contradict the theory are due to the presence of bast soap or boiled-off liquor in the dye-bath.

Tannin Mordant

Tannins have been used for a long time as a mordant, both for cotton and for silk.

Bancroft³ mentions the fact that the "aborigines of North America used sumac as a mordant to fix the red coloring matter of a species of galium on porcupine quills. He also states, p. 117, "that cotton can be dyed with quercitron bark by impregnating the fibre with the astringent matter of myrobolans, rendering to a great extent the use of aluminum acetate unnecessary. In describing the dyeing of cotton with madder, p. 178, he mentions the fact that the cotton can be mordanted first with sumac followed by treatment with alumina. Slater⁴ states that the consumption of galls in printing and dyeing is very limited, being used in the production of the best class of blacks upon silk. He mentions the use of other tannins such as divi-divi, catechu, and sumac in printing and dyeing operations. Dreaper⁵ says that tannic acids are of the greatest value to the dyer of cotton, forming lakes with basic dyes. On silk he believes that they play the part more of a dye than a mordant. Hummel⁶ states that tannic acid acts as a mordant toward coloring matters of basic character such as magenta and malachite green.

Tannins are used on cotton for a mordant largely for basic dyes. The fibre is treated with tannin, for example a decoction of galls, and the adsorbed tannin is fixed by means of tartar emetic. This is necessary in the case of

¹ Pelet-Jolivet: "Die Theorie des Färbeprozesses," 33 (1910).

² J. Phys. Chem., 24, 368 (1924).

³ "Philosophy of Permanent Colors," 2, 76 (1814).

⁴ "Manual of Dye Wares," (1882).

⁵ "Chemistry and Physics of Dyeing," 67 (1906).

⁶ "The Dyeing of Textile Fabrics," 227 (1885).

vegetable fibres for Knecht and Kershaw¹ have shown that tannic acid adsorbed by vegetable fibres is easily washed out by cold water. Georgievics² studied the adsorption of tannin by cotton and concluded that:

(1) The tannin vat never becomes exhausted.

(2) Adsorption depends less upon the actual amount of tannin in solution than upon the concentration. In practice as concentrated a bath as possible is used. Gardner and Carter³ state that the adsorption of tannin by cotton is increased 48-50 percent by the addition of lower fatty acids such as acetic acid. HCl has little or no effect, while sulphuric acid has a detrimental effect. Knecht and Kershaw⁴ studied the adsorption of tannin by cotton under various conditions and they conclude that the best condition for adsorption is to enter the cotton at 100°C and allow to cool with occasional stirring for three hours. They also show that the most tannin is taken up from the more concentrated solutions which is what one should expect.

Tannin is used with silk largely to produce a good grade of black and for weighting by successive alternate treatments with tannin and ferric salt. Vignon⁵ studied the adsorption of tannic acid and gallic acid by silk. He concludes that un gummed silk can adsorb gallic and tannic acids and that the tannic acid is adsorbed more readily than gallic acid, the limit being 25 percent of the weight of the silk. Heermann⁶ also studied the taking up of tannin by silk and states that silk behaves like hide in that it adsorbs a large amount of tannin from cold solutions and as much as 25 percent from a hot solution. He further states that the tannin adsorbed is not readily removed by water. Sisley⁷ studied the effect of the addition of acids on the adsorption of tannin and finds that if silk is stirred in a dilute solution of tannin containing no acid only a small amount of tannin is adsorbed. If mineral acid is present the adsorption is practically complete. He also states that silk will adsorb tannin from more concentrated solution in the absence of acid. He gives no data to show what the effect of acid would be in the case of more concentrated solutions.

Ganswindt⁸ states that of the organic mordants tannin is used to a great extent for silk. He also says, p. 21, that the adsorption from warm baths, (up to 50°C), is purely a mechanical and not a chemical process and that the tannin taken up from such baths can be removed by washing with water and still easier by washing with soap. From hot baths silk can take up 20-25 percent of tannin which is fast to washing and retained firmly even if treated with soap solution.

This paper deals with the adsorption of tannin by silk.

¹ J. Soc. Chem. Ind., 11, 129 (1892).

² Mitt. tech. Gewerbe-Museums in Wien, 8, 1, 362 (1898).

³ J. Soc. Dyers and Colourists 7, 14, 143.

⁴ J. Soc. Chem. Ind., 11, 129 (1892).

⁵ Compt. rend., 121, 916 (1895).

⁶ Färber-Zeitung, 19, 4 (1888).

⁷ Bull., (4) 31, 919 (1908).

⁸ "Theorie und Praxis der modernen Färberei," II, 18 (1903).

Experimental

The silk used in this work was obtained through the courtesy of Professor T. B. Johnson of Yale. The tannins used were J. T. Baker's U. S. P. Tannic Acid, powdered prepared from Chinese nutgalls and Zinsser's U. S. P. Tannic Acid, powdered and Tannic Acid XXX.

One-gram pieces of silk were placed in tannin baths of known composition either at room temperature or at the temperature of the boiling water-bath while attached to a return condenser to prevent evaporation and kept at the required temperature for forty-five minutes. The silk was entered and removed at the temperature maintained throughout the experiment.

The tannin adsorbed was determined by difference after determining the amount of tannin left in the bath at the end of each experiment. The tannin left in the bath was determined by the use of the Loewenthal method.¹ The solutions were standardized against a tannin solution of known concentration.

The effect of temperature on the amount of tannin adsorbed by silk was studied first. The results of a series of experiments are given in Table XV.

TABLE XV

The Effect of Temperature on Adsorption of Tannin by Silk

Volume of bath 100 cc.
Weight of silk 1 g.
Time of experiment 45 minutes

| g. tannin taken | g. tannin adsorbed | |
|-----------------|--------------------|-----------------------------|
| | Room temp. | Temp. of boiling water bath |
| 0.250 | 0.0277 | 0.087 |
| 0.50 | 0.0301 | 0.120 |
| 2.0 | 0.0436 | 0.170 |

These results show clearly that more tannin is taken up by silk at higher temperatures. Knecht² says that the greatest amount of tannin is taken up at the point of incipient boiling.

The effect of varying the concentration was next studied and that data obtained are given in Table XVI.

TABLE XVI

Effect of Concentration on Adsorption of Tannin by Silk

Volume of bath 100 cc.
Weight of silk 1 g.
Temperature Boiling water bath
Time of Experiment 45 minutes

| g. tannin taken | | adsorbed | |
|-----------------|--------|----------|-------|
| 0.125 | 0.025 | 0.50 | 0.100 |
| 0.250 | 0.0551 | 1.00 | 0.150 |
| 0.375 | 0.090 | 2.00 | 0.170 |

¹ J. prakt. Chem., 81, 150 (1860); Z. anal. Chem., 16, 201 (1877); 20, 91 (1881).

² Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 1, 190.

These results show that there is a continual variation in the amount adsorbed, indicating that there is no compound being formed and that the taking up of tannin by silk is an adsorption phenomenon. At least this is true over the range given.

Experiments were next carried out to see if the amount of tannin taken up by the silk from cold tannin baths was a function of time. At the temperature of the boiling water bath forty-five minutes were sufficient to bring about maximum adsorption. At room temperature the amount taken up during the same period was relatively small. It was thought that if at room temperature the silk was left till equilibrium was reached the amount of tannin adsorbed by the silk would undoubtedly be equal to the amount taken up at the higher temperature or might exceed it. Considerable difficulty was met in trying to carry out the experiments over a relatively long period of time. Mould formed in the solutions, usually within a week, making the experiments failures. This difficulty was finally overcome by sterilizing both the solution and the silk, allowing them to cool to room temperature and entering the silk at that temperature. The data obtained are given in Table XVII.

TABLE XVII
Effect of Time on the Adsorption of Tannin by Silk
from Cold Tannin Baths

| g. tannin taken | duration of experiment | temperature | g. tannin adsorbed |
|-----------------|------------------------|--------------------|--------------------|
| 0.25 | 45 minutes | room | 0.0277 |
| 0.25 | 31 days | room | spoiled |
| 0.50 | 45 minutes | room | 0.0301 |
| 0.50 | 31 days | room | 0.0502 |
| 0.50 | 120 days | room | 0.1306 |
| 0.50 | 45 minutes | boiling water bath | 0.1200 |

These results show clearly that the adsorption of tannin by silk from cold baths is a function of time.

The effect of acids on the adsorption of tannin by silk was next studied. Sulphuric acid was used with the dilute solutions so as to prove or disprove the work of Sisley. With more concentrated solutions both sulphuric and acetic acids were tried. The data are given in Table XVIII.

These results show that in dilute solution acid does help in adsorption of tannin but that its effect is not so marked in more concentrated solution.

Finally the effect of washing on the fastness of the tannin adsorbed was studied. Silk that had been treated either in the cold or in the hot was washed with water and a portion of the washed silk treated with a solution of ferric chloride and the depth of the black produced noticed. The remaining

TABLE XVIII
Effect of Acid on Adsorption of Tannin by Silk

| g. tannin taken | cc. N/10 H ₂ SO ₄ | cc. N/10 CH ₃ COOH | g. tannin adsorbed |
|-----------------|-----------------------------------------|-------------------------------|--------------------|
| 0.02 | — | — | 0.002 |
| 0.02 | 40.00 | — | 0.012 |
| 0.50 | — | — | 0.100 |
| 0.50 | 25.00 | — | 0.110 |
| 0.50 | 50.00 | — | 0.120 |
| 0.50 | — | 50.00 | 0.120 |

silk was washed again and the treatment of a portion of the silk so washed repeated with ferric salt and the black produced compared with the first or preceding samples. This process was repeated several times, washing first with water and finally with soap. The silk that had been treated in the cold with the tannin gave up its tannin easily to the water as the inked samples of silk showed. Those silks which had been treated in the hot retained the tannin firmly, even on being washed with soap solution.

Summary

1. A preliminary study has been made of the adsorption of tannin by silk.
2. More tannin is taken up from hot solutions than from cold solutions. If equilibrium is reached in the cold the amount taken up approximates that taken up in the hot.
3. Addition of acids aids to a slight extent in the adsorption of tannin by silk in the hot.
4. Tannin taken up in the cold is fairly easily removed, while tannin taken up in the hot is retained much more firmly.
5. No explanation can be given at present for the effect of temperature on the adsorption of tannin.

Tannin and Electrolytes

Tannins are astringent substances, many of which are glucosides. They exist in the colloidal state in solution.

Tannins are amorphous, slightly acid, and vary in color from dark brown to pure white. They are as a rule peptized by water, alcohol, acetone, ethyl acetate, and glycerol. They are not peptized by chloroform, benzene, petroleum ether, carbon disulphide, and fixed and volatile oils.

Some tannins give blue-black precipitates with ferric salts and others give green-black precipitates. This is generally given as one method of classifying the different tannins.

A large number of inorganic salts precipitate or coagulate tannin solutions. Most tannins give brown precipitations with potassium dichromate.¹ Lime water gives precipitates which vary in color.² Saturated solutions of calcium chloride, sodium chloride, and potassium acetate precipitate them.³ Lead and copper acetates⁴ as well as ammoniacal zinc acetate⁵ have all been used to precipitate tannins in suggested methods of analysis. Stannous chloride,⁶ nickel hydroxide,⁷ and tartar emetic⁸ have also been used to precipitate tannin. Ammonium molybdate precipitates most tannins.⁹ Aluminum oxide¹⁰ has been suggested as a substitute for hide powder in the official method of analysis as adopted by American and English chemists. Other salts which precipitate tannin solutions are ammonium chloride, cobalt acetate, manganese acetate and uranium acetate.

Mineral acids such as hydrochloric and sulphuric acid precipitate tannins but this will be discussed at length later for this paper has to deal with the precipitation of tannins by these two acids.

The tannins in addition to being precipitated by inorganic salts are active reducing agents. They reduce gold and copper solutions and absorb oxygen from the air, especially in alkaline solution. The fact that they are good reducing agents has been made use of in the Loewenthal method of tannin analysis using potassium permanganate.

The glucoside tannins are hydrolyzed by dilute acids yielding glucose as one of the products.

The action of the tannins with mineral acids has been studied since the tannins were first isolated as a new class of substance, about 1790¹¹. Dize¹² first called attention to the precipitate caused by the addition of HCl to an infusion of galls. Davy¹³ mentions the precipitate obtained by acids with tannins. Trommsdorf¹⁴ studied the precipitates formed by the addition of HCl and H₂SO₄ to astringent substances. Berzelius¹⁵ proposed a method of analysis based on the formation of a precipitate with a clear infusion of nut galls by H₂SO₄. Etti in 1887 precipitated oak bark tannin by HCl. Most authors of textbooks in their discussion of tannin state that tannins are pre-

¹ Smith: "Chemistry of Plant Life."

² Allen: "Commercial Organic Analysis," 5.

³ Trimble: "The Tannins," 23 (1922).

⁴ Norris: "Organic Chemistry," 539.

⁵ J. Chem. Soc., 6611, 169 (1894).

⁶ Procter: "Leather Industries Handbook," 103.

⁷ J. Chem. Soc., 11011, 204 (1916).

⁸ J. Soc. Chem Ind., 21, 128 (1902).

⁹ J. Soc. Chem. Ind., 23, 765 (1904).

¹⁰ Allen: "Commercial Organic Analysis", Vol. 5.

¹¹ Trimble: "The Tannins," 1, 9 (1892).

¹² J. Phys., 7, 399.

¹³ Phil. Trans., 93, 233 (1803).

¹⁴ Neu. all. J. Chem. 3, 111 (1804).

¹⁵ Jahresbericht, 7, 244; Lehrbuch, 6, 209 (1837); Pogg. Ann., 10, 257 (1827).

precipitated by dilute mineral acids. Among these authors are to be found Remsen,¹ Norris,² and Behal.³

Thomas and Foster,⁴ with the hopes of throwing some light upon the colloidal nature of tannin, again studied the action of various electrolytes upon numerous tannin extracts. A study of their results brings out the following points:

Oak bark tan liquors are precipitated more and more with increasing acid concentration of hydrochloric acid and sulphuric acid. Acetic acid gives no appreciable precipitation in any case but with higher concentrations the suspended matter begins to dissolve. Formic acid gives similar results. Lactic acid behaves similarly to formic acid but dissolves the suspended matter at lower concentration.

Barium chloride and calcium chloride both give increasing amounts of precipitate with increasing concentration. Aluminum sulphate causes a rapid increase in precipitate, passing through a maximum and then a slower increase.

Wilson⁵ considers these results as a salting out. Thomas and Foster,⁶ in the interpretation of their results, say that the effect of the electrolyte is masked by the salting out and chemical precipitation of molecularly dispersed substances in addition to the colloidal tannins present.

It seemed worth while to determine whether all the tannin of one kind comes out at a given concentration of the precipitating agent as is the case with sols stabilized entirely by an adsorbed ion.

The work of Thomas and Foster was repeated following the method outlined by them. The tannins used were:

(1) U.S.P. Tannic Acid, Powdered, J. T. Baker Chemical Co. This tannin is made from selected Chinese nut-galls.

(2) U.S.P. Tannic Acid, Powdered, Zinsser and Co.

(3) Tannic Acid X.X.X., Zinsser and Co. This last tannin is one of exceptional purity.

Solutions of each tannin were made up so that 100 cubic centimeters of solution contained 4 grams of solid matter. The solutions were made at 85°C, cooled to 35°C and adjusted to final volume. It was found unnecessary with these tannins to centrifuge the stock solution to throw down coarse suspended matter. 25 cc. portions of the stock solution were placed in 50 cc. graduated centrifuge tubes and an equal volume of electrolyte added. The tubes were then centrifuged for five minutes at 1000 times gravity. The volumes of the precipitate were then recorded.

Using hydrochloric acid as the electrolyte the results obtained are given in Table XIX.

¹ "Organic Chemistry," 429 (1922).

² "Traité de Chimie organique," 380.

³ "Organic Chemistry," 180-181, 539.

⁴ J. Ind. Eng. Chem., 14, 194 (1922).

⁵ Wilson: "The Chemistry of Leather Manufacture," 234 (1923).

⁶ J. Ind. Eng. Chem., 14, 194 (1922).

It is seen clearly from Table XIX that no precipitate was obtained with either tannin till a concentration of 2 molar acid was reached in the case of Zinsser's tannic acid. In both cases when precipitation started the volume of precipitate increased with increasing acid concentration. In all cases the precipitates formed with very strong acid varied from those obtained with acids of weaker concentration, by being less dense. This was very noticeable with concentrated acid. These results are shown graphically by Fig. 2, as are also the data obtained by Thomas and Foster. They obtained precipitates with most tannins with acids which were relatively very weak compared with

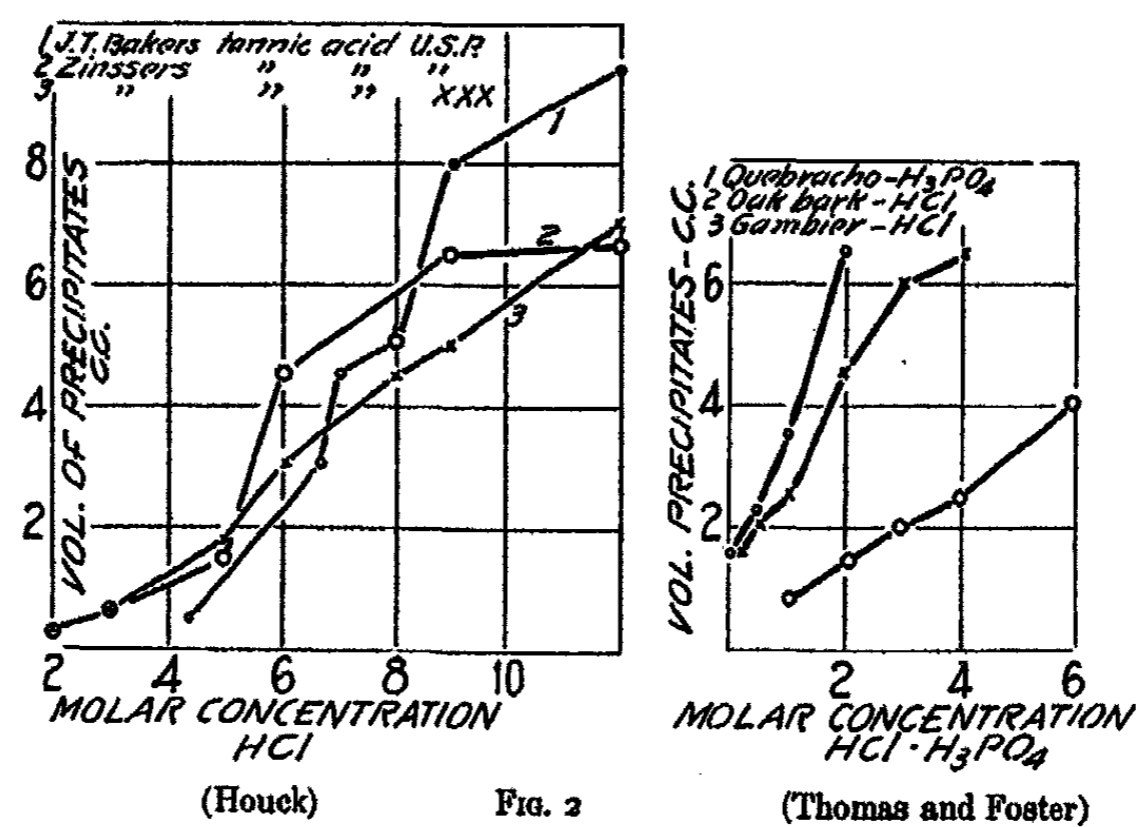


Fig. 2
Precipitation of Tannins

TABLE XIX
Precipitation of Tannins by Hydrochloric Acid

Tannin used 25 cc. of 4 percent solution
Electrolyte used 25 cc.

| Conc. of electrolyte added | Volume of precipitate in cc. | Conc. of electrolyte added | Volume of precipitate in cc. |
|----------------------------|------------------------------|----------------------------|------------------------------|
| | Baker's U.S.P. | | Zinsser's X.X.X. |
| M/100-2 M | 0.00 | M/100-2M | 0.0 |
| 2.0 M | 0.00 | 2 M | 0.25 |
| 3.0 M | 0.00 | 3 M | 0.50 |
| 4.3 M | 0.50 | 4 M | — |
| 5.0 M | — | 5 M | 1.75 |
| 6.6 M | 3.00 | 6 M | 3.00 |
| 7.0 M | 4.5 | 7 M | — |
| 8.0 M | 5.0 | 8 M | 4.5 |
| 9.0 M | 8.0 | 9 M | 5.0 |
| Conc. HCl | 9.5 | Conc. HCl | 7.0 |

the acid of lowest acid concentration precipitating the tannins used during these experiments. With acids of low concentration they were undoubtedly also precipitating foreign matter, other than tannin.

With sulphuric acid as the electrolyte experiments were carried out only with J. T. Baker's Tannic Acid. The results of the experiments are given in Table XX.

TABLE XX

Precipitation J. T. Baker's U.S.P. Tannic Acid, Powdered by Sulphuric Acid

Tannin taken 25 cc. of 4 percent solution
Volume of electrolyte 25 cc.

| Conc. of acid added | Volume of precipitate | Conc. of acid added | Volume of precipitate |
|---------------------|-----------------------|---------------------|-----------------------|
| M/100-2M | 0.0 cc. | 6 M | 10.0 |
| 3M | 0.5 | 7M | 14.0 |
| 4M | 3.0 | 8M | 16.0 |
| 5M | 7.0 | | |

The volume of precipitate formed increased with increasing acid concentration. The difference in the character of the precipitate with stronger acid solutions was very marked here.

Acetic acid did not give a precipitate with any of the three tannins. The acid concentration in this case was varied from 0.005 molar to glacial acetic acid.

Barium chloride did not give a precipitate with Baker's Tannic Acid, U.S.P. powdered or Zinsser's Tannic Acid, U.S.P. powdered. With Zinsser's Tannic Acid X.X.X. a precipitate was obtained with all concentrations of solutions used. The volume of the precipitate was small, 0.25 cc. throughout except with a saturated solution of barium chloride when the volume increased to 0.50 cc.

The character of the precipitate, as noted above, varied with increasing acid concentration. The question immediately arose whether the volume of precipitates obtained with different acid concentrations were comparable with reference to the amount of tannin actually precipitated.

Twenty-five cc. portions of a four percent tannin solution were precipitated with 6M HCl and concentrated HCl respectively and the volumes noted. The precipitates were analyzed for tannin using the Loewenthal method of analysis. The results are given by the following data:

| Precipitant | Volume of precipitate | g. tannin found | Ratio of volumes | Ratio of g. tannin |
|-------------|-----------------------|-----------------|------------------|--------------------|
| 6M HCl | 3.0 cc. | 0.385 | 2.1 | 1.46 |
| conc. HCl | 6.5 | 0.570 | | |

The volume ratio indicates that more than twice as much tannin was precipitated with concentrated HCl as with 6M HCl. The actual amount of tannin precipitated, determined by analysis, was approximately only one and a half times as much with concentrated HCl as with 6M HCl.

It follows from these experiments that the tannin is not precipitated completely at a given concentration of acid and that the volumes of precipitates, obtained with solutions of increasing acid concentration, are not comparable. The volumes of precipitate do not represent the relative amounts of tannin actually precipitated.

These conclusions were confirmed further by other experiments. Tannin was precipitated with acid of a given concentration and then 25 cc. of the filtrate was treated with an equal volume of the same precipitant. In every case more tannin was precipitated. Data obtained are given in Table XXI.

TABLE XXI

Additional Precipitation of Tannin from Original Filtrate by Original Precipitant

Tannin J. T. Baker's U.S.P.

| Precipitant | Volume of precipitate | |
|-------------|-----------------------|----------|
| | Original solution | Filtrate |
| 6M HCl | 2.0 cc. | 0.50 cc. |
| 7M HCl | 3.7 | 0.25 |
| 8M HCl | 4.5 | 0.25 |
| conc. HCl | 6.0 | 0.10 |

Results of the same type and order were obtained using Zinsser's Tannic Acid U.S.P. and Tannic Acid XXX as shown in Table XXII.

TABLE XXII

Additional Precipitation of Tannin from Original Filtrate by Original Precipitant

| Tannin Precipitant | Zinsser's U. S. P. | | Zinsser's X X X | |
|--------------------|--------------------|----------|-----------------|----------|
| | Original | Filtrate | Original | Filtrate |
| 5M HCl | — | — | 1.75 cc. | 0.25 |
| 7M HCl | 3.5 cc. | 0.10 cc. | 3.0 | 0.10 |

The results given in Tables XXI and XXII show that the tannin is precipitated incompletely in the original precipitation.

Incomplete precipitation of the tannin and unreliability in the volume of the precipitates were again shown in another series of experiments. Tannin was precipitated by acid of a given concentration. The precipitate was peptized in water and reprecipitated by acid of the same strength. When the precipitate was completely peptized the volume of precipitate on reprecipitation indicated complete precipitation. Analysis of the precipitates for tannin showed incomplete precipitation. Data obtained in this experiment are given in Table XXIII.

TABLE XXIII

| Tannin | Precipitant | Original Volume | Volume after peptization and re-precipitation | Tannin by analysis | |
|----------------|-------------|-----------------|-----------------------------------------------|--------------------|---------|
| | | | | 1st ppt | 2nd ppt |
| Baker U.S.P. | 6M HCl | 2.5 cc. | 2.5 cc. | | |
| | 7M HCl | 4.5 | 4.5 | 0.539 | 0.376 |
| Zinsser U.S.P. | 7M HCl | 4.0 | 5.0 | 0.595 | 0.397 |

It is evident that the tannin is not precipitated completely and that the volumes obtained do not represent the effect of the electrolyte on the actual amount of tannin precipitated. Hence curves of the type drawn by Thomas and Foster do not represent the effect of the various electrolytes on the actual amount of tannin precipitated. Therefore, the curves are not of much value.

Another source of error which may interfere is hydrolysis. This factor is of greater importance when using mineral acid as the electrolyte. Fischer and Freudenberg¹ state that hydrolysis of a tannin with five percent sulphuric acid at 100°C is nearly complete after 60-70 hours. Hydrolysis would decrease the amount of tannin precipitated.

Summary

Tannins are coagulated by mineral acids and the volume apparently increases with increasing acid concentration. The volumes of tannin coagulated in the experiments described above do not necessarily represent the true effect of the electrolyte because of experimental error due to lack of analysis. The curves of the type drawn by Thomas and Foster are therefore not of any appreciable value. Sources of error in the method of Thomas and Foster are:

(1) The amount of tannin precipitated being determined by volume gives chance for error since the character of the precipitate varies considerably with different factors, such as acid concentration.

(2) The volume of precipitate does not represent the relative amount of tannin precipitated. The volume may be doubled but the actual amount of tannin precipitant may only be slightly increased.

(3) Precipitation is not complete. In some cases the volume relations indicated complete precipitation.

(4) Hydrolysis of the tannin, particularly when mineral acid is used, may result, reducing the volume of the precipitate.

The precipitation of the tannin in the above cases by mineral acids is due to at least two factors:

(1) Adsorption of hydrogen ion.

(2) A decrease in the peptizing action of the water. The peptization of tannin is apparently chiefly a peptization by water and only very slightly an electrical stabilization.

¹ Ber., 45, 922 (1912).

Acknowledgments

To Professor W. D. Bancroft, under whose direction this work was carried on, I desire to express my gratitude for his suggestions and unfailing interest.

It is also a pleasure to acknowledge my debt to my aunt, Miss M. E. Sherman, whose unfailing interest and help has made it possible for me to complete this work.

I also acknowledge gratefully the courtesies of Professor T. B. Johnson of Yale and of Zinsser and Company, who supplied the silk and several tannin samples respectively.

*Cornell University,
April, 1928.*

A FURTHER STUDY OF THE ABSORPTION SPECTRA OF POTASSIUM FERRO- AND FERRICYANIDES

BY FREDERICK H. GETMAN

In a former paper on the absorption spectra of the ferro- and ferricyanides of potassium¹ it was pointed out that the absorption spectra of the so-called α and β ferrocyanides described by Briggs² are identical, thereby furnishing additional evidence in support of the claim made by Bennett³ that these salts are not isomeric.

It was also pointed out that a slight but nevertheless well-defined difference exists between the absorption spectra of the α and β ferricyanides of potassium described by Locke and Edwards.⁴

It may be recalled that these investigators were the first to show that when a solution of ordinary red, or α - $K_3Fe(CN)_6$, is treated with a dilute acid and then precipitated with alcohol, an olive-green salt, corresponding to the formula, $K_3Fe(CN)_6 \cdot H_2O$, is formed. This salt they designated as β potassium ferricyanide. This salt was shown by its discoverers to differ in many of its reactions from the ordinary, or α potassium ferricyanide. For example, on treating a solution of the β -salt with a dilute solution of bismuth nitrate no precipitate is formed, whereas when the ordinary or α -salt is similarly treated with bismuth nitrate a copious yellow precipitate is thrown down. Notwithstanding the attempts of Bellucci and Sabatini⁵ on the one hand, and of Hauser and Biesalski⁶ on the other, to disprove the statements of Locke and Edwards relative to the existence of these two modifications of potassium ferricyanide, the work of the latter investigators was completely confirmed by Wells who repeated their experiments with great care and convinced himself of the correctness of their conclusions.

While the results of our earlier spectroscopic study of these substances are thus seen to be in perfect agreement with the contention that Briggs' so-called α and β ferrocyanides do not exist, whereas the α and β ferricyanides of Locke and Edwards are well-defined chemical compounds, it has seemed desirable to repeat our work with more refined apparatus. In our earlier studies the absorption spectra were photographed by means of a small Hilger quartz spectrograph, size E₃₁, and the resulting plates were measured and the absorption curves mapped by the familiar method of Hartley and Baly. In the present work a large Hilger quartz spectrograph, size E₃, with wave-length scale, was used in conjunction with a Judd Lewis sector photo-

¹ Getman: *J. Phys. Chem.*, 25, 147 (1921).

² Briggs: *J. Chem. Soc.*, 99, 1019 (1911).

³ Bennett: *J. Chem. Soc.*, 111, 490 (1917).

⁴ Locke and Edwards: *Am. Chem. J.*, 21, 193, 413 (1899).

⁵ Bellucci and Sabatini: *Atti. Accad. Lincei*, 23I, 176 (1911).

⁶ Hauser and Biesalski: *Ber.*, 45, 2516 (1912).

meter to determine the curves of absorption. The tilt of the camera of the spectrograph was adjusted by preliminary trials with a copper spark until the readings of the wave-length scale agreed with the values of the wave-lengths of the principal lines of the copper spectrum as given in a table of standard wave-lengths. In all of the subsequent experiments a condensed

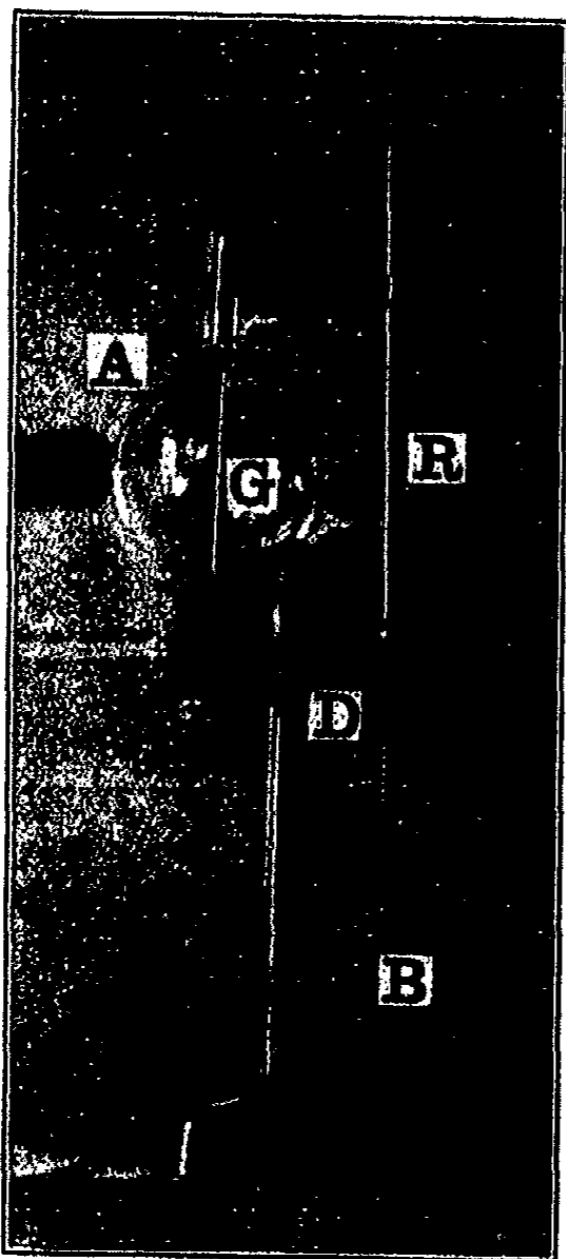


FIG. 1

spark between nickel-steel electrodes was used as the source of ultra-violet radiation. In order to make sure that no narrow absorption bands had escaped notice, owing to discontinuities in the iron-nickel spectrum, a source of continuous ultra-violet radiation was employed with the spectrograph alone.

An apparatus similar in principle to that devised by Fulweiler and Barnes¹ was constructed in which an electric discharge between tungsten wires under water constituted the source of continuous ultra-violet radiation extending to $\lambda_2 = 210 \mu\mu$. In the production of the spark discharge, the primary terminals of a $\frac{1}{4}$ kilowatt transformer specially designed for spectrum work were connected with the 110 volt A. C. lighting circuit. The secondary terminals were connected with two $\frac{1}{4}$ kilowatt condensers in parallel, each condenser having a capacity of approximately 0.03 microfarad. An adjustable spark gap, against which a current of air was directed by means of a small rotary blower, was joined in series with the tungsten electrodes. The tungsten wires forming the electrodes were 2 mm. in diameter and were so arranged

that the length of the spark gap could be easily adjusted by means of regulating screws. The most satisfactory length of spark under the electrical conditions which prevailed was found to be approximately 0.5 mm. With the slit of the spectrograph adjusted to 0.05 mm., a two minute exposure was found ample to give a thoroughly satisfactory spectrogram.

The special mounting shown in Fig. 1 was developed in the course of this investigation and because of its convenience in bringing the source of radiation into final adjustment we digress for a brief description of its salient features. By means of clamps attached to the vertical rod, R, the specially designed Pyrex flask, A, carrying the spark gap, G, was fastened at approximately the correct height before the slit of the spectrograph.

¹ Fulweiler and Barnes: J. Franklin Inst., 194, 83 (1922).

The final adjustment was effected by means of the screw, B, which operates against the spiral spring, C. A similar adjustment in a horizontal plane can be made by means of the screw, D.

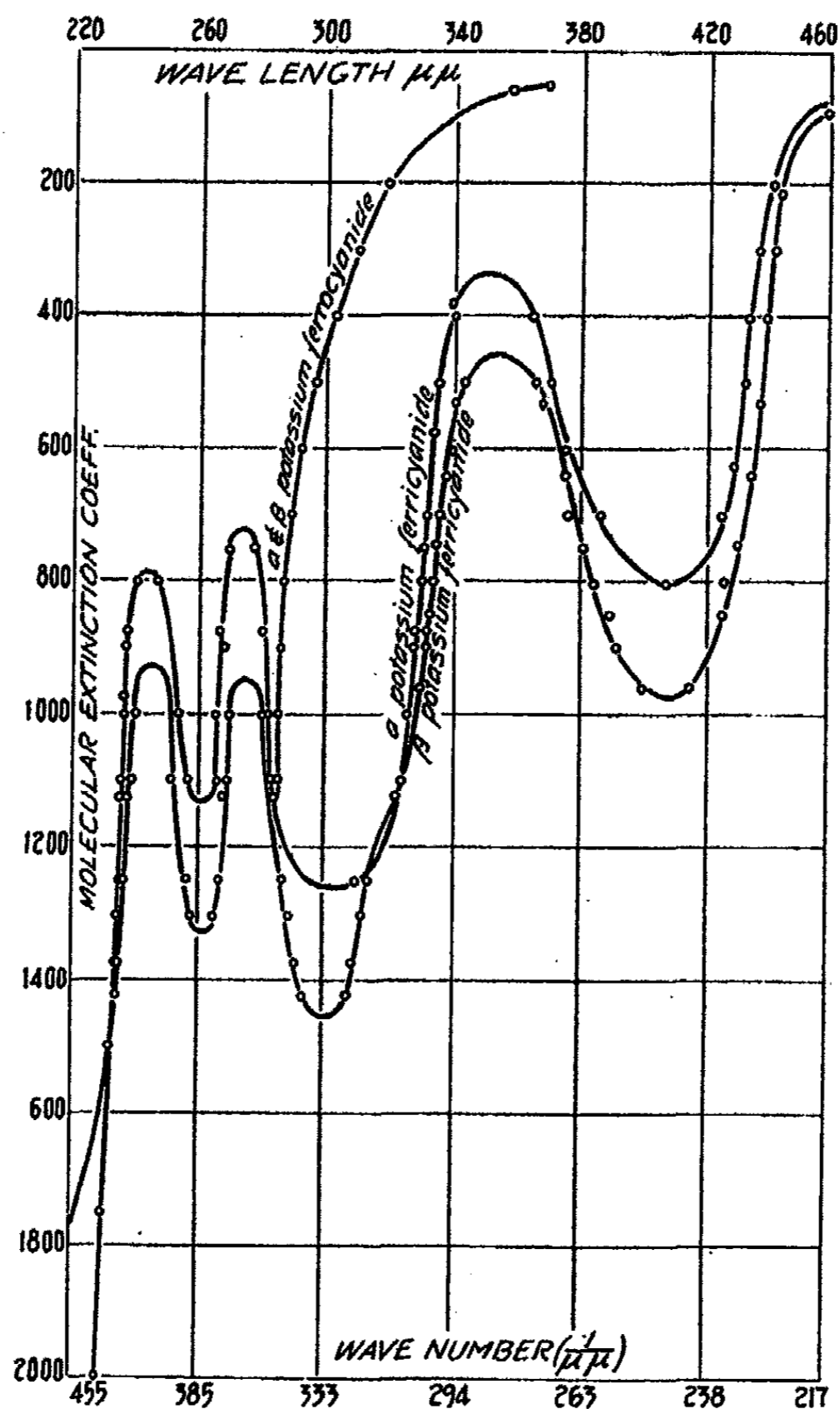


FIG. 2

The methods employed in the preparation of the salts and the procedure followed in making up the solutions were similar to those described in our earlier paper.

The measurements of the plates obtained with the spectrograph and sector photometer are represented graphically in Fig. 2, where molecular extinction coefficients are plotted as ordinates against the corresponding wave-lengths (or their reciprocals, known as wave-numbers) as abscissae. Employing ab-

sorption tubes 20 mm. in length, it was found that the optimum concentration for complete mapping of the absorption curves of both the ferro- and ferricyanides was 0.0005 molar.

It will be observed that the absorption curves of the so-called α and β ferrocyanides of potassium are coincident. While thus confirming the conclusions drawn from our previous examination of the absorption spectra of these two substances, a comparison of the actual curves of absorption established by the two series of experiments reveals a marked disagreement between them. The experimental method employed in the earlier work, how-



FIG. 3

- | | | |
|-----|--------------------------------|----------------------------------------------|
| (A) | Spectrum of source. | |
| (B) | Absorption spectrum of 0.0005N | α -K ₄ Fe(CN) ₆ |
| (C) | " | β -K ₄ Fe(CN) ₆ |
| (D) | " | α -K ₃ Fe(CN) ₆ |
| (E) | " | β -K ₃ Fe(CN) ₆ |

ever, being little better than qualitative, we believe that the curve shown in Fig. 2 may be accepted as representing the variation of absorption with changing wave-length of incident radiation within the limits of experimental error.

In our earlier study of the absorption of ultra-violet radiation by the α and β ferricyanides of potassium we were led to believe that a well-defined although slight difference exists in the absorptive properties of these two salts. The data which we have now obtained with the spectrophotometer leaves no doubt as to the validity of our former statement. As in the case of the ferrocyanides, however, the actual form of the absorption curves is found to be quite different from that previously plotted from measurements of the plates by the so-called Baly method.

Owing to the relatively sparse distribution of lines in those regions of the iron-nickel spectrum where it was especially desired to confirm the existence of absorption bands in solutions of both ferro- and ferricyanides, the tungsten spark under water was employed. As has already been stated, this source of ultra-violet radiation gives a continuous spectrum to $\lambda = 210\mu\mu$. By means of this source it was possible to secure spectrograms which confirmed in a most satisfactory manner the existence and position of the absorption bands. In Fig. 3 is shown a spectrogram obtained with 0.0005 molar solutions of α and β ferrocyanides and α and β ferricyanides in tubes 40 mm. long. The

spectrum immediately below the scale is that of the source alone, while the succeeding spectra correspond to α ferricyanide, β ferricyanide, α ferrocyanide and β ferrocyanide respectively. That a marked difference exists between the absorption spectra of the ferro- and ferricyanides is clearly shown by the spectra in Fig. 3.

Summary

The results of further spectroscopic examination of the ferro- and ferricyanides of potassium contained in the foregoing pages may be briefly summarized as follows:

(1) The molecular extinction coefficients of the compounds designated by Briggs as α and β ferrocyanides of potassium have been determined and found to be identical. This result supports the view advanced by Bennett that these salts are not isomeric as claimed by Briggs.

(2) In like manner the molecular extinction coefficients of the α and β ferricyanides of potassium have been determined and found to be appreciably different from each other, thereby confirming the statement of Locke and Edwards as to the probable isomerism of these two compounds.

(3) An apparatus for producing sparks under water between tungsten electrodes has been employed in a further examination of solutions of the ferro- and ferricyanides with a view to detecting any narrow or weak absorption bands which might otherwise have been overlooked within the spectral range involved.

(4) The absorption spectra of the ferro- and ferricyanides of potassium have been shown to differ markedly from each other.

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298A-27

THE CATALYTIC ACTIVITY OF METALLIZED SILICA GELS

IV. The Oxidation of Methane

BY L. H. REYERSON AND L. E. SWEARINGEN

A great many investigations have been carried out having as their basis the oxidation of methane. The researches of Bone and Wheeler and their co-workers are well known. In recent years Berl and Fischer¹ have studied the oxidation of methane at temperatures above 400°. They find small amounts of formaldehyde under certain conditions. Tropsch and Rollen² also studied this reaction passing the mixed gases through heated quartz tubes at rather rapid rates. The best results obtained by these investigators corresponded to a conversion of about six per cent of the total methane to formaldehyde. Because of the interest which attaches to the oxidation of methane it was thought that a study of the activity of metallized silica gels on this reaction might lead to interesting results in the field of partial oxidation of hydrocarbons.

Experimental

The same experimental procedure was used in this work and the same catalysts used as in the previous paper by the authors on the synthesis of water. A gas absorption pipette containing a solution of KOH was added to the gas analysis system to take care of the CO₂ formed by oxidation. The gases were streamed at rates varying from 15 cc. to 200 cc. per minute through an apparent volume of 500 cc. of catalyst. The reaction was studied with the catalyst maintained at temperatures varying from 200° to 400°. The gases after reaction were analysed for carbon dioxide and oxygen. Preliminary experiments showed that the only oxidation product of methane present in analizable quantity was carbon dioxide.

Results

The results of the experiments are given in Tables I to IV and in Fig. 1. The symbols used have the following meaning:

- A—The percent of methane in the original mixture.
- O₂—The percent of oxygen in the original mixture.
- A'—The percent of methane in the exit gas.
- O₂'—The percent of oxygen in the exit gas.
- f—The fraction of the exit gas found to be CO₂.
- F—The percent of the exit gas found to be CO₂.
- x—The fraction of the original methane oxidized.
- X—The percent of the original methane oxidized.
- A''—The calculated percent of methane in the exit gas.
- O₂''—The calculated percent of oxygen in the exit gas.

¹ Z. angew. Chem., 36, 297 (1923).

² Brennstoff Chem., 5, 37 (1924).

In the following reaction, $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ if the fraction of methane oxidized is x , then the percent of methane in the gas mixture after the reaction is given by

$$A'' = \frac{100(A - Ax)}{(A + O_2 - 2Ax)} \quad (1)$$

Likewise the percent of O_2 in the final mixture is

$$O_2'' = \frac{100(O_2 - 2Ax)}{(A + O_2 - 2Ax)} \quad (2)$$

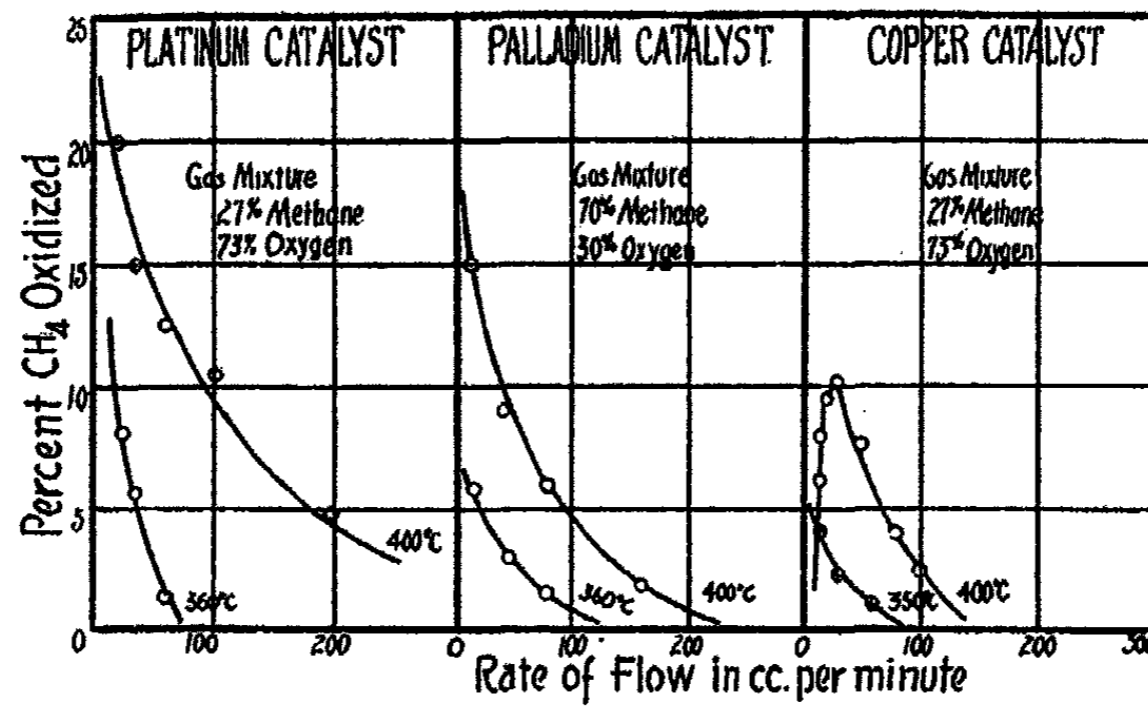


FIG. 1
Rate-Conversion Curves for the Oxidation of Methane

The percent of CO_2 in the gases after reaction is given by

$$F = \frac{Ax}{(100 - 2Ax)} \quad (3)$$

where $F = 100 f$.

It is evident that the amount of methane oxidized is equal to the amount of carbon dioxide formed. For the value of x we have

$$x = \frac{100f}{A + 2Af} \quad (5)$$

Substituting the value of x from (4) in (1) and (2) we have

$$A'' = A + f(2A - 100)$$

and

$$O_2'' = O_2 + 2f(O_2 - 100)$$

The values of A'' and O_2'' given in the tables are calculated from the experimental value because f is determined experimentally. The value of O_2' was determined experimentally and the value of A' was determined by difference. The values in the tables are expressed in percentage.

TABLE I
Silver Catalyst

Gas Mixture: (A) Methane 72.30% (O₂) Oxygen 27.70%.

| Temp. °C | Rate c.c. per minute | Final Analysis | | | | Calculated from F | |
|-------------|----------------------------|----------------|------------------|------|------|-------------------|----------------------|
| | | A' | O ₂ ' | F | 100x | A' | O ₂ ' |
| 360 | 45 | 83.69 | 10.28 | 6.03 | 7.46 | 74.65 | 20.32 |
| 360 | 45 | 72.58 | 27.15 | 0.27 | 0.37 | 72.12 | 27.61 |
| 360 | 45 | 72.30 | 27.70 | 0.00 | 0.00 | 72.30 | 27.70 |
| 360 | 45 | 72.43 | 27.03 | 0.54 | 0.74 | 72.24 | 27.22 |
| 360 | 45 | 72.45 | 26.70 | 0.85 | 1.16 | 72.37 | 26.78 |
| 250 | 45 | 98.64 | 1.36 | 0.00 | 0.00 | 72.30 | 27.70 |
| 250 | 45 | 73.50 | 26.50 | 0.00 | 0.00 | 72.30 | 27.70 ²⁵⁰ |
| 250 | 45 | 72.30 | 27.70 | 0.00 | 0.0 | 72.30 | 27.70 |
| 200 | 45 | 99.69 | 0.31 | 0.00 | 0.0 | 72.30 | 27.70 |
| 200 | 45 | 86.37 | 13.50 | 0.00 | 0.0 | 72.50 | 27.70 |
| 200 | 45 | 71.30 | 27.70 | 0.00 | 0.0 | 72.30 | 27.70 |
| 200 | 45 | 71.82 | 27.90 | 0.28 | 0.4 | 72.12 | 27.60 |

TABLE II
Copper Catalyst

Gas Mixture: (A) Methane 69.00% (O₂) Oxygen 31.00%.

| Temp. °C | Rate c.c. per Minute | Final Gas Analysis | | | | Calculated from F | |
|-------------|----------------------------|--------------------|------------------|-------|-------|-------------------|------------------|
| | | A' | O ₂ ' | F | 100x | A' | O ₂ ' |
| 400° | 15 | 75.12 | 12.60 | 12.28 | 14.29 | 73.67 | 14.10 |
| 390 | 12 | 73.75 | 17.65 | 8.60 | 10.65 | 72.26 | 19.12 |
| 390 | 25 | 71.25 | 20.45 | 7.80 | 9.79 | 71.96 | 20.24 |
| 390 | 45 | 70.94 | 25.80 | 3.36 | 4.57 | 70.28 | 26.40 |
| 390 | 75 | 69.75 | 26.32 | 2.93 | 4.00 | 70.11 | 26.93 |
| 390 | 200 | 69.12 | 28.90 | 1.98 | 2.76 | 69.75 | 28.20 |
| 400 | 200 | 70.12 | 28.00 | 1.88 | 2.63 | 69.71 | 28.40 |
| 360 | 15 | 71.98 | 22.05 | 5.97 | 7.73 | 71.27 | 22.70 |
| 360 | 15 | 70.63 | 23.25 | 6.12 | 7.90 | 71.32 | 22.55 |
| 360 | 200 | 70.00 | 28.95 | 1.05 | 1.49 | 69.40 | 29.50 |
| 320 | 15 | 70.86 | 26.90 | 2.24 | 3.11 | 69.85 | 27.90 |
| 320 | 200 | 69.21 | 29.45 | 1.34 | 1.89 | 69.50 | 29.16 |

Gas Mixture: (A) Methane 76.00%, Oxygen 24.00%

| | | | | | | | |
|-----|-----|-------|-------|------|------|-------|-------|
| 380 | 12 | 91.96 | 4.67 | 3.37 | 4.14 | 77.75 | 18.88 |
| 380 | 35 | 79.77 | 13.18 | 7.05 | 8.14 | 79.66 | 13.29 |
| 380 | 40 | 80.13 | 13.60 | 6.27 | 7.34 | 79.26 | 14.47 |
| 380 | 45 | 78.33 | 17.55 | 4.12 | 5.01 | 78.14 | 17.74 |
| 380 | 60 | 77.52 | 20.00 | 2.48 | 3.12 | 77.29 | 20.23 |
| 380 | 100 | 77.23 | 21.10 | 1.67 | 2.12 | 76.87 | 21.46 |
| 380 | 200 | 76.15 | 22.90 | 0.95 | 1.25 | 76.49 | 22.56 |

TABLE II (Continued)
Copper Catalyst

| Temp. Rate | | Final Gas Analysis | | | | Calculated from F | |
|-----------------------------------------------------------------|-----------------|--------------------|------------------|------|-------|-------------------|------------------|
| °C | o.s. per minute | A' | O ₂ ' | F | 100x | A' | O ₂ ' |
| Gas Mixture: (A) Methane 27.00% (O ₂) Oxygen 73.00% | | | | | | | |
| Gas Mixture: Methane 27.00%, Oxygen 73.00% | | | | | | | |
| 400°C. | 15 | 42.16 | 56.71 | 1.13 | 4.10 | 26.48 | 72.39 |
| 400 | 15 | 30.76 | 67.48 | 1.76 | 6.30 | 26.19 | 72.05 |
| 400 | 15 | 27.23 | 70.67 | 2.10 | 7.45 | 26.03 | 71.87 |
| 400 | 20 | 26.39 | 70.91 | 2.70 | 9.50 | 25.76 | 71.54 |
| 400 | 30 | 26.09 | 71.00 | 2.91 | 10.20 | 25.66 | 71.333 |
| 400 | 50 | 26.51 | 71.10 | 2.39 | 7.60 | 26.02 | 71.59 |
| 400 | 80 | 26.82 | 72.08 | 1.20 | 4.00 | 26.49 | 72.41 |
| 400 | 100 | 26.03 | 72.31 | 0.66 | 2.40 | 26.70 | 72.64 |
| 400 | 15 | 26.48 | 71.70 | 1.82 | 7.26 | 26.16 | 72.02 |
| 400 | 15 | 26.72 | 72.50 | 1.78 | 7.12 | 26.18 | 72.04 |
| 400 | 45 | 26.68 | 71.82 | 1.50 | 6.05 | 26.31 | 72.19 |
| 400 | 75 | 27.10 | 72.15 | 0.56 | 2.30 | 26.74 | 72.70 |
| 350 | 15 | 26.78 | 72.10 | 1.12 | 4.07 | 26.48 | 72.40 |
| 350 | 15 | 26.35 | 72.47 | 1.18 | 4.26 | 26.46 | 72.36 |
| 350 | 30 | 27.04 | 72.30 | 0.66 | 2.40 | 26.70 | 72.64 |
| 350 | 60 | 27.18 | 72.50 | 0.32 | 1.20 | 26.85 | 72.83 |
| 350 | 15 | 55.50 | 43.70 | 0.80 | 2.90 | 26.63 | 72.57 |
| 350 | 15 | 36.56 | 62.30 | 1.14 | 4.10 | 26.48 | 72.38 |
| 350 | 15 | 27.77 | 70.00 | 2.23 | 7.90 | 25.97 | 71.80 |
| 350 | 30 | 26.73 | 71.82 | 1.45 | 5.20 | 26.33 | 72.22 |
| 350 | 60 | 27.06 | 72.20 | 0.74 | 2.70 | 26.66 | 72.60 |
| Gas Mixture: Methane 76.00%, Oxygen 24.00% | | | | | | | |
| 390 | 150 | 94.67 | 3.20 | 2.13 | 2.69 | 77.11 | 20.76 |
| 390 | 150 | 82.30 | 11.00 | 6.70 | 7.77 | 79.48 | 13.82 |
| 390 | 150 | 78.00 | 18.28 | 3.72 | 4.55 | 77.93 | 18.35 |
| 390 | 150 | 78.47 | 16.90 | 4.63 | 5.56 | 78.40 | 16.97 |
| 340 | 32 | 97.22 | 2.50 | 0.28 | 0.37 | 76.15 | 23.57 |
| 340 | 32 | 77.92 | 21.00 | 1.08 | 1.39 | 76.56 | 22.36 |
| 340 | 32 | 76.65 | 22.05 | 1.30 | 1.67 | 76.67 | 22.03 |
| 340 | 32 | 76.49 | 22.45 | 1.06 | 1.37 | 76.55 | 22.39 |
| 340 | 32 | 76.55 | 22.15 | 1.30 | 1.67 | 76.67 | 22.03 |
| 340 | 32 | 76.38 | 22.05 | 1.57 | 2.03 | 76.82 | 21.61 |
| 340 | 32 | 76.74 | 20.90 | 2.36 | 2.97 | 77.23 | 20.41 |
| 340 | 32 | 76.76 | 21.90 | 1.34 | 1.72 | 76.70 | 21.96 |
| 340 | 32 | 76.85 | 21.05 | 2.10 | 2.67 | 77.09 | 20.81 |

TABLE II (Continued)

Copper Catalyst

Gas Mixture: Methane 76.00%, Oxygen 24.00%

| Temp. °C | Rate c.c. per minute | Final Gas Analysis | | | | Calculated from F | |
|-------------|----------------------------|--------------------|------------------|------|------|-------------------|-------------------|
| | | A' | O ₂ ' | F | 100x | A'' | O ₂ '' |
| 200 | 50 | 99.46 | 0.54 | 0.00 | 0.00 | 76.00 | 24.00 |
| 200 | 50 | 80.63 | 18.85 | 0.52 | 0.68 | 76.27 | 23.21 |
| 200 | 50 | 76.53 | 22.95 | 0.52 | 0.68 | 76.27 | 23.21 |
| 200 | 50 | 76.16 | 23.30 | 0.54 | 0.70 | 76.28 | 23.18 |
| 200 | 50 | 76.14 | 23.40 | 0.46 | 0.60 | 76.24 | 23.30 |
| 200 | 50 | 76.05 | 23.25 | 0.70 | 0.90 | 76.36 | 23.00 |
| 360 | 45 | 99.31 | 0.28 | 0.41 | 0.54 | 76.21 | 23.31 |
| 360 | 45 | 80.00 | 17.40 | 2.60 | 3.25 | 77.35 | 20.05 |
| 360 | 45 | 76.78 | 21.30 | 1.92 | 2.35 | 77.00 | 21.08 |
| 360 | 45 | 76.57 | 21.80 | 1.63 | 2.08 | 76.85 | 21.52 |
| 360 | 45 | 76.58 | 22.10 | 1.32 | 1.69 | 76.69 | 21.39 |
| 360 | 45 | 76.38 | 22.04 | 1.38 | 1.77 | 76.72 | 21.90 |
| 360 | 45 | 76.35 | 22.30 | 1.35 | 1.73 | 76.70 | 21.95 |

TABLE III

Platinum Catalyst

Gas Mixture: (A) Methane 80.00% (O₂) Oxygen 20.00%

| Temp. °C | Rate c.c. per minute | Final Gas Analysis | | | | Calculated from F | |
|-------------|----------------------------|--------------------|------------------|-------|-------|-------------------|-------------------|
| | | A' | O ₂ ' | F | 100x | A'' | O ₂ '' |
| 365 | 25 | 86.39 | 3.06 | 10.55 | 11.93 | 86.33 | 3.12 |
| 365 | 25 | 87.66 | 0.00 | 12.50 | 12.50 | 87.50 | 0.00 |
| 365 | 45 | 87.50 | 0.00 | 12.34 | 12.38 | 87.40 | 0.26 |
| 365 | 100 | 87.24 | 0.69 | 12.07 | 12.14 | 87.24 | 0.69 |
| 365 | 200 | 87.24 | 0.74 | 11.92 | 12.04 | 87.15 | 0.93 |
| 330 | 15 | 87.52 | 0.18 | 12.30 | 12.35 | 87.38 | 0.32 |
| 330 | 25 | 87.22 | 0.58 | 12.20 | 12.26 | 87.32 | 0.46 |
| 330 | 45 | 86.95 | 0.77 | 12.28 | 12.32 | 87.37 | 0.35 |
| 330 | 100 | 86.82 | 0.98 | 11.60 | 11.77 | 86.96 | 1.44 |
| 330 | 200 | 86.46 | 2.26 | 11.28 | 11.50 | 86.77 | 1.95 |
| 250 | 20 | 82.94 | 12.80 | 4.26 | 4.90 | 82.56 | 13.18 |
| 250 | 40 | 81.40 | 16.95 | 1.65 | 2.00 | 80.99 | 17.36 |
| 250 | 65 | 81.02 | 18.15 | 0.83 | 1.02 | 80.50 | 18.67 |

Gas Mixture: (A) 78.00% Methane, (O₂) 22.00% Oxygen

| | | | | | | | |
|-----|-----|-------|------|-------|-------|-------|------|
| 300 | 20 | 84.60 | 2.15 | 13.25 | 13.43 | 85.41 | 1.34 |
| 300 | 30 | 84.77 | 2.91 | 12.32 | 12.85 | 84.80 | 2.88 |
| 300 | 80 | 84.15 | 5.17 | 10.68 | 11.28 | 83.90 | 5.40 |
| 300 | 100 | 83.83 | 5.26 | 10.90 | 11.48 | 84.10 | 5.00 |
| 300 | 200 | 85.01 | 3.04 | 11.95 | 12.35 | 87.40 | 3.35 |

TABLE III (Continued)

Platinum Catalyst

| Temp. °C | Rate c.c. per minute | Final Gas Analysis | | | | Calculated from F | |
|------------------------------------------------------------------|----------------------------|--------------------|------------------|-------|-------|-------------------|------------------|
| | | A' | O ₂ ' | F | 100x | A' | O ₂ ' |
| Gas Mixture: (A) 27.00% Methane, (O ₂) 73.00% Oxygen | | | | | | | |
| 360 | 25 | 26.40 | 71.30 | 2.30 | 8.15 | 25.94 | 71.76 |
| 360 | 35 | 26.13 | 72.30 | 1.57 | 5.65 | 26.29 | 72.14 |
| 360 | 60 | 26.72 | 73.00 | 0.38 | 1.40 | 26.88 | 72.74 |
| 360 | 200 | 27.00 | 73.00 | 0.00 | 0.00 | 27.00 | 73.00 |
| 400 | 20 | 24.78 | 69.10 | 6.12 | 20.20 | 24.18 | 69.70 |
| 400 | 35 | 26.25 | 69.30 | 4.45 | 15.10 | 24.95 | 70.60 |
| 400 | 60 | 26.29 | 70.10 | 3.61 | 12.50 | 25.34 | 71.05 |
| 400 | 100 | 26.39 | 70.60 | 3.01 | 10.50 | 25.64 | 71.38 |
| 400 | 200 | 26.86 | 71.80 | 1.34 | 4.80 | 26.38 | 72.28 |
| 330 | 25 | 26.40 | 73.20 | 0.40 | 1.47 | 26.82 | 72.78 |
| 330 | 25 | 26.56 | 72.55 | 0.59 | 2.16 | 26.73 | 72.68 |
| 330 | 25 | 26.84 | 72.55 | 0.61 | 2.20 | 26.72 | 72.67 |
| Gas Mixture: (A) 72.00% Methane, (O ₂) 28.00 Oxygen | | | | | | | |
| 400°C. | 25 | 80.80 | 0.00 | 19.20 | 19.30 | 80.43 | 0.37 |
| 400 | 50 | 80.72 | 0.28 | 19.00 | 19.10 | 80.36 | 0.37 |
| 400 | 90 | 80.67 | 0.28 | 19.15 | 19.20 | 80.33 | 0.57 |
| 400 | 150 | 80.74 | 0.56 | 18.70 | 18.95 | 80.23 | 1.07 |
| 400 | 200 | 80.67 | 0.28 | 19.05 | 19.15 | 80.38 | 0.57 |
| 360 | 45 | 80.92 | 0.00 | 19.08 | 19.20 | 80.40 | 0.52 |
| 360 | 80 | 80.80 | 0.14 | 19.20 | 19.28 | 80.45 | 0.35 |
| 360 | 100 | 80.35 | 1.00 | 18.65 | 18.89 | 80.20 | 1.15 |
| 360 | 150 | 80.40 | 0.80 | 18.80 | 19.00 | 80.26 | 0.94 |
| 320 | 45 | 80.86 | 0.14 | 19.00 | 19.10 | 80.35 | 0.65 |
| 320 | 80 | 80.73 | 0.27 | 19.00 | 19.10 | 80.35 | 0.65 |
| 320 | 100 | 80.43 | 1.57 | 18.00 | 18.40 | 79.92 | 2.08 |
| 320 | 150 | 80.12 | 2.08 | 17.80 | 18.20 | 79.83 | 2.37 |
| 275 | 45 | 80.54 | 1.11 | 18.35 | 18.82 | 80.60 | 1.05 |
| 275 | 45 | 80.43 | 0.97 | 18.60 | 18.85 | 80.18 | 1.22 |
| 245 | 45 | 73.75 | 21.95 | 4.30 | 5.52 | 73.89 | 21.81 |

TABLE IV

Palladium Catalyst

Gas Mixture: (A) Methane 70.00% (O₂) Oxygen 20.00%

| Temp. | Rate c.c. per minute | Final Gas Analysis | | | Calculated from F | | |
|-------|----------------------------|--------------------|------------------|-------|-------------------|-------|-------------------|
| | | A' | O ₂ ' | F | 100x | A'' | O ₂ '' |
| 400 | 15 | 74.92 | 12.28 | 12.80 | 14.56 | 75.13 | 12.07 |
| 400 | 15 | 75.12 | 11.58 | 13.30 | 15.00 | 75.33 | 11.27 |
| 400 | 40 | 73.24 | 20.40 | 7.21 | 9.00 | 72.89 | 19.90 |
| 400 | 80 | 71.33 | 23.60 | 4.57 | 5.98 | 71.83 | 23.60 |
| 400 | 160 | 70.00 | 28.40 | 1.44 | 2.00 | 69.42 | 27.98 |
| 360 | 15 | 71.05 | 24.69 | 4.55 | 5.72 | 71.74 | 23.91 |
| 360 | 45 | 70.00 | 26.75 | 2.19 | 3.00 | 69.12 | 28.67 |
| 360 | 80 | 70.31 | 28.60 | 1.09 | 1.55 | 70.44 | 28.47 |

Gas Mixture: (A) Methane 71.50% (O₂) 28.50%

| | | | | | | | |
|-----|----|-------|-------|------|------|-------|-------|
| 360 | 20 | 73.08 | 23.75 | 3.17 | 4.18 | 72.86 | 23.97 |
| 360 | 40 | 72.90 | 24.70 | 2.40 | 3.21 | 72.53 | 25.07 |
| 360 | 40 | 72.80 | 24.70 | 2.50 | 3.33 | 72.57 | 24.93 |
| 335 | 20 | 72.34 | 26.60 | 1.06 | 1.41 | 71.95 | 26.99 |
| 335 | 30 | 72.27 | 26.80 | 0.93 | 1.28 | 71.90 | 27.17 |
| 335 | 45 | 72.34 | 26.80 | 0.86 | 1.18 | 71.87 | 27.27 |

Gas Mixture: (A) Methane 27.00%, Oxygen 73.00%

| | | | | | | | |
|--------|-----|-------|-------|------|-------|-------|-------|
| 400°C. | 15 | 25.47 | 69.50 | 5.03 | 16.90 | 24.69 | 70.28 |
| 400 | 30 | 26.15 | 70.00 | 3.85 | 13.10 | 25.23 | 70.92 |
| 400 | 45 | 26.40 | 71.05 | 2.55 | 9.00 | 25.82 | 71.83 |
| 400 | 90 | 26.88 | 71.00 | 2.12 | 7.52 | 26.01 | 71.86 |
| 400 | 150 | 27.03 | 71.70 | 1.27 | 4.60 | 26.42 | 72.31 |
| 400 | 200 | 26.97 | 72.20 | 0.83 | 3.00 | 26.62 | 72.55 |
| 360 | 15 | 26.45 | 72.00 | 2.24 | 7.95 | 26.97 | 71.79 |
| 360 | 20 | 26.59 | 72.05 | 1.36 | 4.90 | 26.38 | 72.26 |
| 360 | 30 | 26.19 | 73.00 | 0.81 | 2.95 | 26.63 | 72.56 |
| 360 | 100 | 26.45 | 73.15 | 0.40 | 1.47 | 26.72 | 72.88 |
| 330 | 15 | 26.55 | 72.00 | 1.45 | 5.21 | 26.35 | 72.22 |
| 330 | 20 | 27.09 | 72.10 | 0.81 | 2.95 | 26.63 | 72.56 |
| 330 | 40 | 27.08 | 72.40 | 0.52 | 1.90 | 26.76 | 72.72 |
| 330 | 60 | 27.45 | 72.25 | 0.30 | 1.10 | 26.86 | 72.84 |

Discussion of Results

The results for the copper and silver catalyst are very interesting. It is evident in the case of both of these catalysts that in the early stages of the reaction oxygen is being removed from the gas stream and that this oxygen is not used in the oxidation of methane. This is indicated in Tables I and II when successive samplings are made at the same streaming rate. After the first removal of oxygen the silver catalyst shows practically zero activity throughout the temperature range studied while the copper continues to show catalytic activity. Because of this removal of oxygen in the early

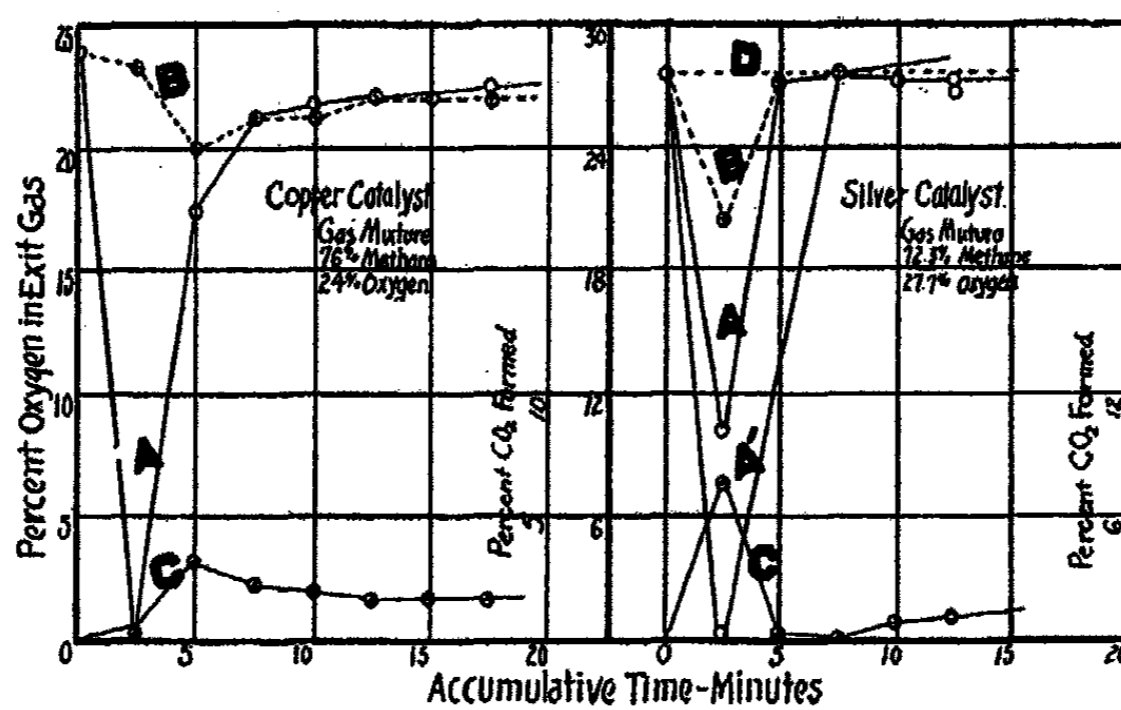


FIG. 2
 Time Efficiency Curves—Oxidation of Methane

stages of reaction additional experiments were carried out. With the aid of a by pass tube around the catalyst samples were collected and analysed at $2\frac{1}{2}$ minute intervals. The results of these experiments are shown graphically in Fig. 2. In the case of the copper catalyst the temperature was 360° while in the case of the silver the curves for both 360° and 200° are given. Curves A in the case of both catalysts give the amounts of oxygen found in the gases after reaction at 360° . Curves B are for the oxygen calculated to be present from the amount of CO_2 formed and curves C are for the amounts of CO_2 found in the exit gases. Curve A' for silver is for the amount of oxygen found at 200° and Curve D gives the calculated oxygen content at 200° from the CO_2 found. There was no CO_2 found at 200° so D gives the value for the O_2 in the original gas mixture.

These experiments show quite definitely that the oxygen, which first reaches the copper and silver deposited on the silica gel, is taken up by these metals almost completely. It may be strongly adsorbed or else combined chemically to form the oxide. Since it is impossible to differentiate between these two states at present it is easier to conclude that chemical combination has taken place. In the case of copper it is probably another case where the copper must be partially oxidized before it will act as a catalyst in oxidations.

This accounts for the strange shape of the curve for the copper catalyst at 400° as shown in Fig. 1. The first measurements were made on a fresh catalyst and the first three points are those taken successively at about the same rate of flow. After reaching an equilibrium state of oxidation the catalyst behaved just as the platinum and palladium catalysts. In order to account for the rather large amount of CO₂ produced initially at 360° in the case of the silver catalyst one has to assume that the silver was acting as an oxidizing catalyst prior to being oxidized itself or else there was some adsorbed CO₂ in the catalyst. This does not seem reasonable because there was none found at 200° where adsorption should be better than at 360°. The instability of silver oxide at higher temperatures accounts for the fact that more oxygen was removed at 200°.

In the case of the platinized gel no such removal of oxygen was observed in the initial stages of reaction. The reaction seems to quickly reach an equilibrium state. Furthermore, the rate of streaming does not have much effect on the efficiency of the reaction as long as the methane is in excess. The reaction becomes measurable at about 240°. Small increases in oxygen content produce increases in the amount of oxidation. This does not hold over the total range of concentrations because an excess of oxygen does not produce complete oxidation. In fact the catalyst is less sufficient when the oxygen content is high than when it is low. For example a change from twenty to twenty-eight percent in the oxygen content of the gas sample increased the amount of methane oxidized from about twelve percent to more than nineteen percent. On the other hand an oxygen content of seventy-three percent only gives an oxidation of eight percent and the efficiency of the catalyst falls off rapidly as the rate of gas flow increases. As in other catalytic studies there is apparently a definite concentration ratio of oxygen to methane which will produce the best results. These experiments also indicate that the methane must reach the catalyst surface before it is oxidized.

In the case of the palladium catalyst the reaction does not become measurable until 330° or nearly 100° above that at which the platinized gel causes oxidation. The same general results were obtained for the palladium catalyst as for the platinum except that the palladium was less efficient at a given temperature Table IV shows that increases in the oxygen content at low concentrations of oxygen causes more reaction while oxygen in excess leads to lessened reaction. The difference in the efficiency between the platinum and palladium may be due to the fact that the platinized gel is a slightly better adsorbent of oxygen. This is shown in the adsorption studies¹ on these gels.

Summary

1. With the exception of the silver catalyst the metallized silica gels have been shown to act catalytically in the oxidation of methane. They promote the complete oxidation of methane, yielding carbon dioxide and water. No partial oxidation products were found.

¹ Reyerson and Swearingen: *J. Phys. Chem.*, 31, 88 (1927).

2. The copper catalyst is apparently oxidized to a considerable extent and then the copper oxide or the copper, copper oxide acts as the catalyst. The copper catalyst starts the reaction at a temperature as low as 200°.

3. The efficiency of the platinum and palladium catalysts depends upon the oxygen content of the gas mixture.

4. The platinized gel initiates reaction at a temperature as low as 240° while the palladium does not become active until about 330°. The platinized gel was found to be the most active of the catalysts in this reaction.

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FACTORS AFFECTING THE COAGULATION OF COLLOIDAL CLAY

BY RICHARD BRADFIELD*

Extensive field experiments are now in progress in many countries for testing the effect of different coagulating agents upon the physical properties and productivity of agricultural soils. It has long been known that the application of the divalent calcium ion in sufficient quantity will bring about an improvement in soil structure which is in general regarded as due to a decrease in the degree of dispersion of the colloidal clay. The coagulation of clay by electrolytes has been much studied in the laboratory, but due partly to the great differences in the soils themselves, to differences in the methods used, and to the presence of uncontrolled variables our knowledge regarding the fundamental nature of the process is still extremely meagre.

An attempt has been made at the Missouri Laboratory to isolate some of these variables and to determine their effect under controlled conditions. It has been shown, in the case of acid clays, that very slight changes in the pH value obtained after mixing the electrolyte and the clay cause a very great change in coagulation value especially near the neutral point (1). With neutral or alkaline soils this effect is of course less pronounced (2). It has also been shown that in certain cases at least the nature of the anion has a specific influence that can not be attributed to changes in the hydrogen ion concentration. The coagulation value has been found to depend in a peculiar way upon the concentration of the clay sol. With a neutral salt like CaCl_2 or KCl the coagulation value is almost independent of the concentration of the clay, while in the case of the hydroxides of these metals the value increases in direct proportion to the concentration of the clay. Mixtures of the neutral salt and the hydroxide give values which, in general, tend to agree with one or the other or both constituents, depending upon the pH value produced.

The experiments just cited were carried out with a colloidal clay sol separated from the Putnam silt loam subsoil by means of the Sharples Laboratory Supercentrifuge by a method previously described (3). This natural sol contains from twenty-five to thirty milliequivalents of exchangeable bases per 100 grams of clay, of which about fifty percent are Ca, fifteen percent Mg and the rest largely Na and K. The sol contains from twenty-two to twenty-five milliequivalents of exchangeable H per 100 grams. The average saturation capacity of the colloid is from fifty-two to fifty-five milliequivalents per 100 grams. When we consider that the Ca ion is about ten times as efficient as a coagulating agent as the K ion, and that the former is readily displaced by the latter when the latter is introduced in the form of a neutral salt, it would seem quite natural to expect that the coagulation values obtained would be greatly affected by this exchange reaction. This has been found to be the case for other clays by Wiegner and Gallay (4).

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Information regarding the role played by exchange reactions during the coagulation process can be obtained by conducting two parallel series of experiments in one of which the exchange reactions are allowed to proceed normally while in the other these reactions are either prevented or controlled.

It has been shown recently that a soil can be easily freed from exchangeable bases and saturated with hydrogen ions by electro dialysis (3). The reaction involved is apparently a simple hydrolysis of the surface ions of the alumino-silicate complex. If the calcium-saturated complex is represented as CaX then the reaction involved in electro dialysis is expressed by the equation:



The resulting electro dialyzed clay (H_2X) is well suited for coagulation studies because (1) it is free from ordinary electrolytes, (2) it is free from exchangeable bases, and (3) it may be easily saturated to any desired extent with any base by the addition of the proper amount of the proper hydroxide.

Experimental Method

Preparation of materials. The colloidal clay was separated from the subsoil of the Putnam silt loam by the method previously described. This sol was made up of particles under 100μ in diameter. The electro dialysis was carried out in an ordinary three-compartment cell between parchment membranes, using a platinum gauze anode and a nickel gauze cathode. A potential of 150 volts was applied to the electrodes and the dialysate was siphoned off periodically and replaced by distilled water. The dialysis was continued until the catholyte was free from bases. This required in most cases four to six days. The electro dialyzed clay was suspended in distilled water, the concentration determined by the pycnometer method and a series of dilute solutions prepared from this stock solution. The six percent stock solution had a pH value of 3.2 to 3.4 and a total acidity equivalent to fifty-five milliequivalents per 100 grams dry clay.

Determination of coagulation values. The coagulation values were determined by the same method used in the earlier experiments (1) using the concentric tube device suggested by Weiser except that in this case a smaller apparatus was used. Five cc. of the clay sol was measured into the outer space by means of a pipet, the desired amount of electrolyte was then measured into the center tube, and sufficient water added to bring the volume up to five cc. The clay and the electrolyte were then thoroughly mixed by inverting the cell quickly. After a thoro shaking, the mixture of clay and electrolyte was poured into test tubes and allowed to stand for fifteen minutes. The test tubes were then centrifuged for an additional fifteen minutes. The minimum concentration of electrolyte required to produce complete coagulation could in most cases be determined easily and fairly accurately by this method. The coagulation value is expressed in every case in terms of milliequivalents of Ca or K per liter. In most cases no difficulty was encountered in reproducing results. In every case the values plotted in the curves represent the average of at least four closely agreeing determinations.

Experimental Results

The effect of electro dialysis upon the coagulation values obtained with $\text{Ca}(\text{OH})_2$ are shown in Fig. 1. With this divalent base the coagulation value is a linear function of the concentration of the clay. (Curves A and B). The saturation curves C and D represent the amount of $\text{Ca}(\text{OH})_2$ required to neutralize the acidity of the colloidal clay as determined by potentiometric titration. In the case of $\text{Ca}(\text{OH})_2$ the increase in coagulation values resulting from

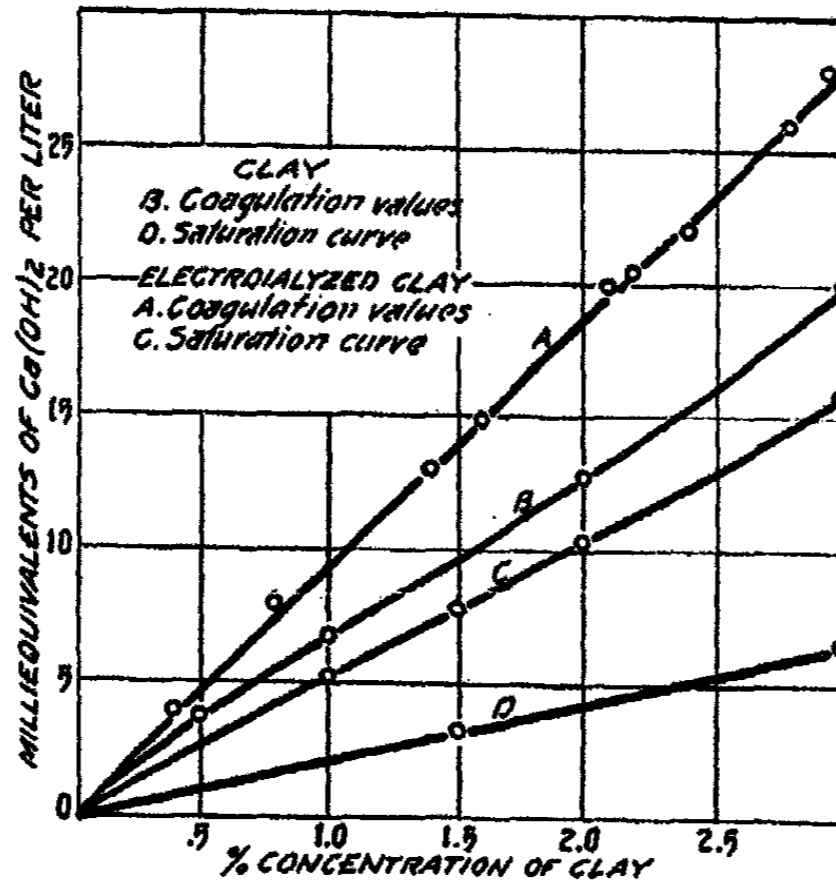


FIG. 1

Effect of concentration of the clay sol upon the coagulation values of clay before (B) and after (A) electro dialysis. Coagulating agent $\text{Ca}(\text{OH})_2$.

electro dialysis can be largely accounted for by the difference in the degree of saturation of the clay. In the case of both the natural and the electro dialyzed sol the coagulation values are about double the saturation values. When KOH is used as the coagulating agent (Fig. 2), the effect of electro dialysis is much greater than it was with $\text{Ca}(\text{OH})_2$. This was of course expected as the bases removed by electro dialysis were largely Ca and Mg. The coagulation values increase with the concentration of the clay, but not linearly as in the case of $\text{Ca}(\text{OH})_2$. No explanation has been found for the upward inflexion on curve A. The influence of electro dialysis is most marked at the lower concentrations. In the case of the .25 percent sol (Concentration of clay is always expressed as concentration resulting after mixing with electrolyte) the coagulation value was increased from twenty-two to one hundred three as a result of electro dialysis. This shows quite conclusively the very important role that exchange reactions may play in coagulation phenomena. The difference between the coagulation values and saturation values are much greater in the case of KOH than with $\text{Ca}(\text{OH})_2$. The electrokinetic potential

of a potassium clay is much greater than that of a calcium clay and consequently a much greater excess of that cation is necessary to lower the potential to the critical value.

With the neutral salts of both KCl and CaCl₂ the coagulation values are practically independent of the concentration of the clay. (See KCl curve Fig. 3.) With mixtures of the bases and their neutral salts very complex

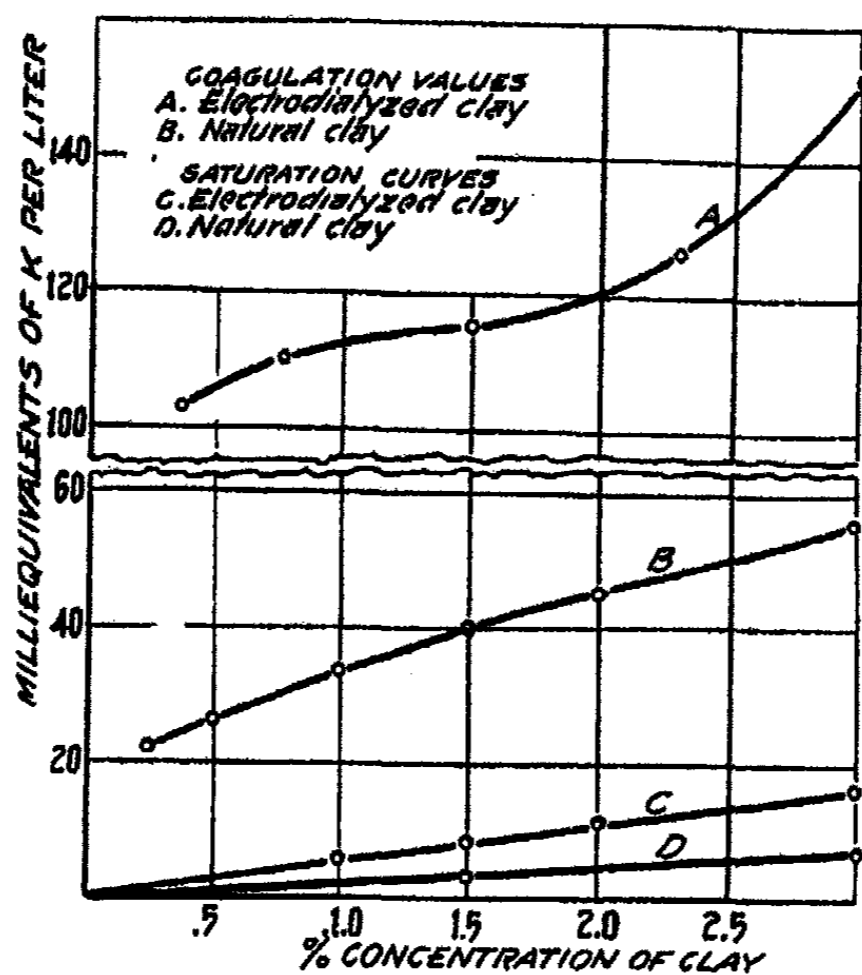


FIG. 2

Coagulation values of natural and electrolyzed colloidal clay with KOH as influenced by the concentration of the clay.

curves may be obtained. With a mixture of eight parts KCl and two parts KOH for instance, the coagulation values obtained with the .25 percent and the .50 percent sols are almost the same as those obtained with KOH alone, while with all clay sols above 1.5 percent the values obtained with this mixture are almost identical with those obtained with KCl alone. Quite frequently two different coagulation values could be found for the same electrolyte mixture, one of which was of the same order of magnitude as that of the neutral salt alone while the other approached that of the alkali alone. This anomalous behavior was in every case related to the pH value of the mixture. If a sufficient concentration of the cation were present to bring about coagulation at pH values less than six, then values similar to the neutral salt were obtained. If, however, sufficient base were present to render the mixture alkaline then values similar to those obtained with the pure base were obtained.

The effect of hydrogen ion concentration was even more pronounced in the case of the electrolyzed clay (Fig. 4) than it was in the case of the natural sol (Fig. 3). In Fig. 4 are shown the coagulation values as a function of the

final pH value. The values for the most dilute (.25%) and the most concentrated (3%) sols both before and after electro dialysis are shown. In the case of the electro dialyzed clay all the points are segregated into two very distinct zones. The first is an acid zone with pH values under five and coagulation values under five milliequivalents per liter. The second is an alkaline zone with pH values between eleven and thirteen and coagulation values between one hundred six and one hundred eighty. No distinct coagulation values were obtained between these two zones.

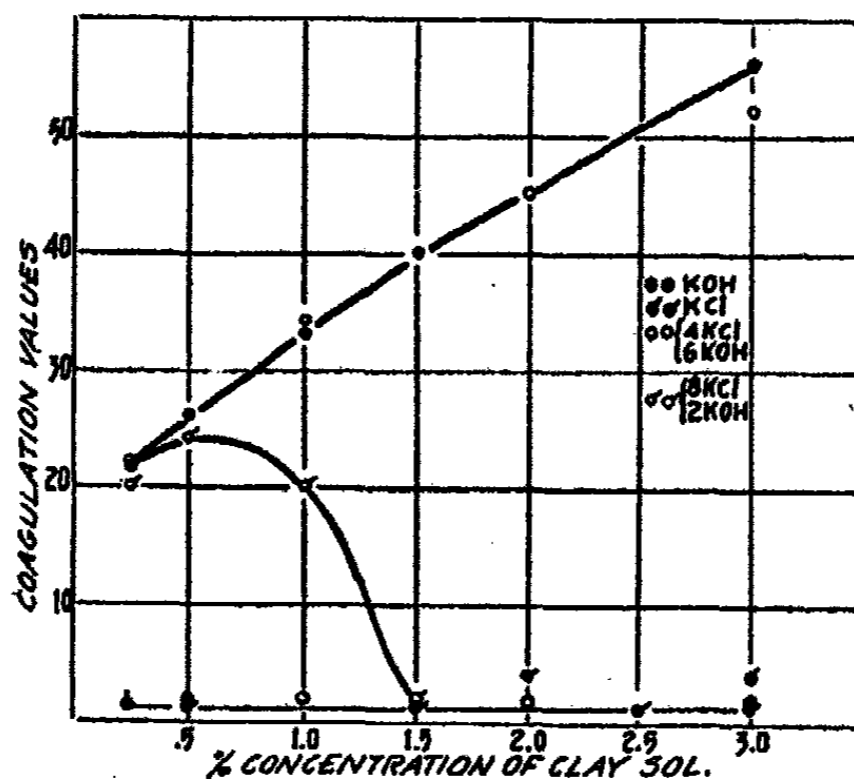


FIG. 3

Effect of concentration of clay sol upon coagulation values obtained with KCl, KOH and mixtures of these solutions.

With the natural clay there is also a tendency toward a low acid and a high alkaline coagulation zone. The zones are, however, much wider in pH range. With the .25 percent natural clay the coagulation values were constant between the pH values nine and twelve.

Discussion of Results

These experiments show quite conclusively that the coagulation value of a colloidal clay may vary widely with slight changes in either: (1) hydrogen-ion concentration, (2) concentration of the clay sol, or (3) in the nature and extent of the exchange reactions which take place when the coagulating agent is mixed with the clay. The effect of hydrogen-ion concentration is most marked when exchange reactions are prevented by the use of sols freed from exchangeable bases by electro dialysis. The two distinct critical pH value zones found with this purified clay are probably due to the fact that in the acid region the hydrogen clay which has a very small electrokinetic potential is being flocculated while in the alkaline region the potassium or calcium clay with much higher charges on the particle is involved. Two distinct consecutive reactions probably take place in the case of coagulation in an alkaline

medium. (1) The acidity of the clay itself must first be neutralized. The amount of base required for this purpose is, of course, directly proportional to the concentration of the clay. (2) A sufficient excess of electrolyte must then be added to coagulate the resulting Ca- or K-saturated clay. In the case of $\text{Ca}(\text{OH})_2$ the amount of base required for the neutralization of the acidity of

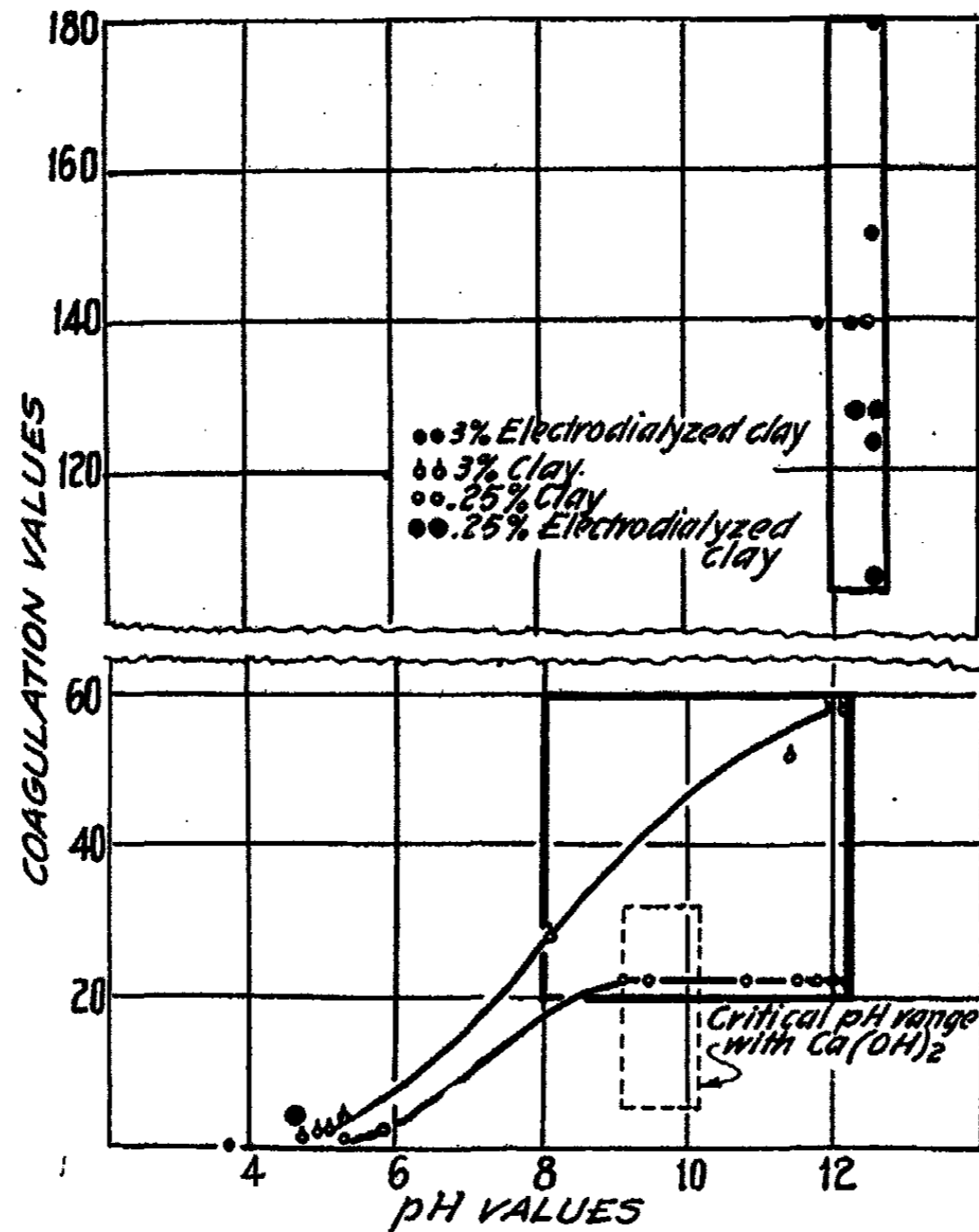


FIG. 4

Effect of pH value on the coagulation values—clay sols before and after electro dialysis. Coagulating agents, KCl , KOH and mixtures of these solutions.

the clay constitutes about 60% of the total required for coagulation. With KOH , however, the neutralization is responsible for 10 percent or less, (depending on concentration of the clay) of the total electrolyte requirement. This may be attributed either to specific differences in the absorbability of the two cations or possibly to differences in the amount of ionization at the surface of the particle. At any rate the cataphoretic potential of the potassium clay is much higher than that of the calcium clay, and a higher concentration of electrolyte is necessary to bring it to the critical point.

The effect of the concentration of the clay sol upon coagulation values proved to be quite complex. Only the monovalent K and divalent Ca ions were studied. With the neutral salts of these bases the values were practically independent of the concentration of the sol. With $\text{Ca}(\text{OH})_2$ the critical concentration was a direct linear function of the concentration of sol. With the KOH the values increased but not nearly as rapidly as with $\text{Ca}(\text{OH})_2$. When various mixtures of the bases and their neutral salts were used as coagulants very complex curves were obtained. The clever explanation offered by Kruyt (5) for the effects observed by earlier investigators of this problem will have to be amplified if they are to clarify satisfactorily all the observations made in this study.

The effect of exchange reactions upon coagulation values has been but little studied in the past. The very striking differences observed in the behavior of the natural clay and the electrolyzed clay sols show quite clearly, however, that these reactions may be of great importance.

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A STUDY OF THE POTENTIALS AND ACTIVITIES OF THE METALS IN ZINC AMALGAM CELLS

BY J. N. PEARCE AND J. F. EVERSOLE

Electromotive force measurements of zinc amalgam cells have been made by Richards and Forbes,¹ Richards, Wilson and Garrod-Thomas² and by Hulett and Crenshaw.³ In these investigations different methods were used in preparing and handling the amalgams, but both were designed to give re-

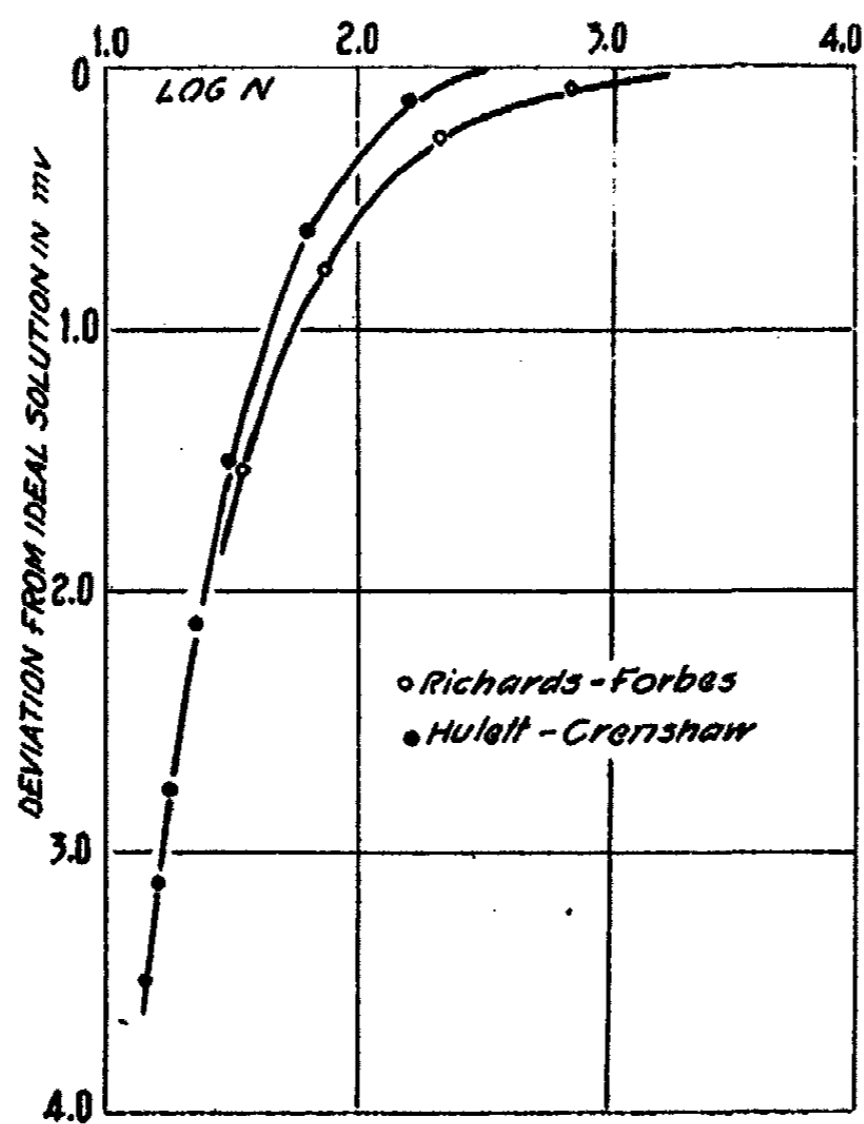


FIG. 1

sults of a high degree of accuracy. There is, however, an unfortunate lack of agreement between the results obtained in the two laboratories. This is best shown by Fig. 1. All attempts to bring them into harmony, or to point out errors in either method of procedure, have failed.

Richards and his co-workers have measured the electromotive forces existing between various dilute amalgams in contact with a saturated solution

¹ Richards and Forbes: Pub. Carnegie Inst., 56; Z. physik. Chem., 58, 683 (1907).

² Richards, Wilson and Garrod-Thomas: Pub. Carnegie Inst., 118, Z. physik. Chem., 72, 129, 165 (1909).

³ Hulett and Crenshaw: J. Phys. Chem., 14, 175 (1910).

of zinc sulphate. They have also calculated the potentials which the amalgams would have, if they formed perfect solutions. For this calculation they used the familiar relation,

$$E = \frac{RT}{nf} \ln \frac{c_1}{c_2} \quad (1)$$

in which c_1 and c_2 denote the respective concentrations of the zinc in the amalgams. They have found that the observed potentials are less than those calculated by (1), and, further, that the deviations from the calculated values increase as the concentration of the zinc in the amalgam is continuously increased.

In a similar study at 25° Hulett and Crenshaw have measured the electromotive forces of zinc amalgam cells over a concentration range, extending from the saturated two-phase amalgam to very dilute amalgams. In each case the potential was measured against the constant, easily reproducible two-phase amalgam. They found that for the range, 0.0061 N - 0.00000307 N, the potential between any two amalgams conforms to the laws of a perfect solution, as indicated by (1). The fact that these amalgams do appear to behave as perfect solutions for a given range of concentration and that they then suddenly become imperfect is difficult to comprehend.

Hildebrand¹ has measured the vapor pressure of mercury over zinc amalgams at 325°. From the results obtained he seems to have shown conclusively that zinc dissolved in mercury is polymerized according to the equilibrium relation, $2 \text{Zn} \rightleftharpoons \text{Zn}_2$. Applying the law of mass action, using mol fractions instead of concentrations, this equilibrium is given accurately by the equation,

$$K \left(\frac{1 + 2\alpha}{N + 1 - \alpha} \right)^2 = \frac{\alpha}{N + 1 - \alpha} \quad (1)$$

where N is the number of mols of mercury to one mol of zinc, α is the number of Zn_2 mols and K is the equilibrium constant. In this work he has assumed that the type of equilibrium existing is independent of the temperature, but that the value of the equilibrium constant changes with the temperature.

In a later work,² Hildebrand has shown that the electromotive force of a concentration cell containing liquid zinc amalgams is accurately given by the relation,

$$nE_f = RT \int_{N_1}^{N_2} \frac{N_2}{N_1} \ln p, \quad (2)$$

By means of a series of mathematical deductions and substitutions, involving the Raoult vapor pressure law and equations (1a) and (2), he arrives finally at the equation,

$$E = 0.00019834 \frac{T}{n} \log \frac{1 + N_2 + \sqrt{N_2 + 2AN_2 + A}}{1 + N_1 + \sqrt{N_1 + 2AN_1 + A}} \quad (3)$$

¹ Hildebrand: *Trans. Am. Electrochem. Soc.*, 32, 335 (1912).

² Hildebrand: *J. Am. Chem. Soc.*, 35, 501 (1913).

In this n is the valence and N is the number of mols of mercury to one mol of zinc. $A = 4K + 1$, where K is the equilibrium constant of (1a). Hildebrand tested the validity of equation (3), using the electromotive force data collected by Richards and Forbes at 23.01° . For this he let $A = 11.6$, which implies a value of $K = 2.65$. The values of E thus calculated, and the observed values were found to agree within the limit of experimental error. He also calculated from his vapor pressure data the potentials which the same cells should have, if the zinc were not associated. In such cases, according

to the vapor pressure law, $p = p_0 \frac{N}{N+1}$, we find

$$N d \ln p = \frac{dN}{N+1},$$

which, on integration and substitution of the ordinary values of the constants, gives the relation,

$$E = 0.00019834 \frac{T}{n} \log \frac{N_2 + 1}{N_1 + 1}. \quad (4)$$

This equation follows directly from (3) in case the zinc were not associated, that is, when $K = 0$, and, therefore, when $A = 1$. When Hildebrand applied equations (3) and (4) to the data of Hulett and Crenshaw he found that, while the deviations from the ideal potentials are not far from those corresponding to the work of Richards and Forbes and to equations (3), the difference is, nevertheless, far greater than the maximum error claimed by the investigators. Moreover, he found that no value can be assigned to A which will bring the measurements of Hulett and Crenshaw into harmony with the theory.

In view of the discrepancies arising in the works of the investigators cited, we thought it worth while to repeat the study of the electromotive forces of zinc amalgam electrodes. To this end we have followed, in general, the procedure of Hulett and Crenshaw.

Materials and Apparatus

Mercury—The mercury used in this work was purified by repeated spraying through dilute nitric acid, then dried by heating and fractionally distilled five times in a current of air under reduced pressure. It was finally dried by heating in an electric oven at 105° and stored in a vacuum desiccator.

Zinc Sulphate.—The zinc sulphate was purified by digesting Baker's "Analyzed" salt with zinc oxide and hydrogen peroxide to oxidize any ferrous iron. The solution was then filtered, made slightly alkaline with ammonia and hydrogen sulphide was added until a fairly heavy precipitate of zinc sulphide was formed. This mixture was digested for two days on a steam bath, then cooled and filtered. This procedure should remove any heavy metals which might have been present. The zinc sulphate was then allowed to crystallize, and it was subsequently recrystallized three times, the last time from conductivity water. The salt thus purified was used in preparing the electrolyte for the cells and also in preparing the zinc for the amalgams.

Zinc.—The zinc was prepared by the electrolysis of solutions of the purified zinc sulphate, using a cathode consisting of a 0.5 mm. tip of a small platinum wire sealed into the end of a glass tube. The current density was kept low so that a rather compact deposit of zinc was formed. The solution was kept neutral during electrolysis by surrounding the large platinum anode with a porous cup, filled with basic zinc sulphate prepared from the purified salt. The zinc obtained by electrolysis was washed, dried and twice fused

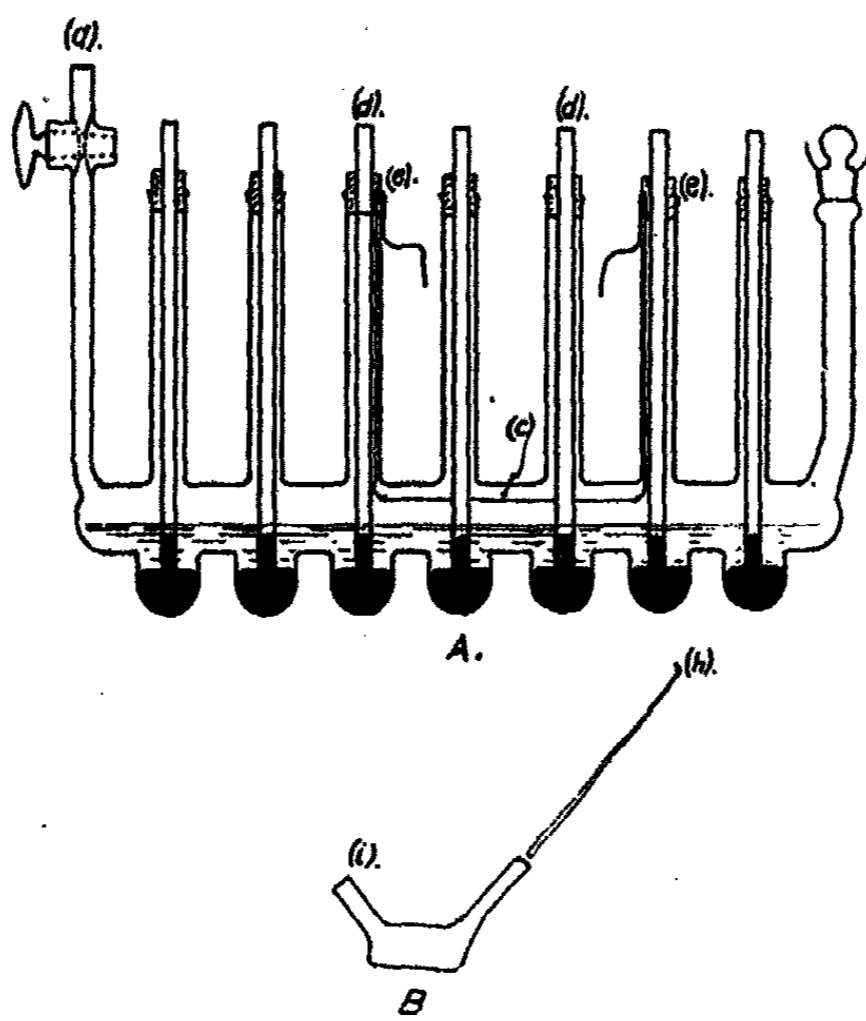


FIG. 2

with pure solid ammonium chloride to remove the occluded mother liquor. It was then distilled four times under reduced pressure in a Pyrex glass tube, the last distillation being made in an atmosphere of hydrogen. Under these conditions, no fog, due to oxidation, appeared as was the case when air was used instead of hydrogen. The bright crystalline zinc was then cut to convenient size by means of a clean steel "side cutters."

Hydrogen.—The hydrogen was prepared by the electrolysis of a strong solution of sodium hydroxide between nickel gauze electrodes. It was bubbled through an alkaline solution of pyrogallol to remove oxygen and then through a tower containing fused calcium chloride and soda lime.

The electrode vessels, eight in number, were made of Pyrex glass and were of the form shown in Fig. 2. In preparing a cell for use the cell was filled to about three quarters of its capacity with a solution of zinc sulphate, saturated at 25°, and the solution was then boiled for a short time under reduced pressure. The tube was then repeatedly filled with hydrogen and repeatedly evacuated. Finally, to remove the last traces of oxygen, the solution was

subjected to a long period of continuous stirring, accompanied by an intermittent glowing of the platinum wire, *c*. To prepare the amalgam the mercury was weighed in a special pipette, Fig. 2, B, and was introduced into one of the cups of the cell under hydrogen pressure. This was done by removing an electrode tube by breaking the cement seal at *d*, lowering the capillary of the pipette into the cell and breaking off the capillary tip at *h* by pressure against the bottom of the cell. The zinc was weighed accurately and then dropped into the mercury. During these operations a rapid stream of hydrogen was passed into the cell at *a* and out through the opening through which the addition was made. Amalgams made up in this manner have been kept for eight months without any evidence of surface oxidation.

The weights of mercury used are accurate to 0.10 mg., those of zinc to 0.01 mg. Each cell when made up contained one amalgam with exactly 2.22 g. of zinc in 100 g. of mercury. This gives a two-phase amalgam at 25°, and it is the amalgam against which the potential of each of the other electrodes was read.

All potential measurements were made by means of a high resistance, 5-dial Wolff potentiometer in series with a sensitive Leeds and Northrup galvanometer. By means of galvanometer deflections it was possible to read the potentials to ± 0.001 mv. The cells were immersed in a large oil thermostat which was electrically controlled to $\pm 0.01^\circ$ at any desired temperature. The temperatures were read by means of a standard thermometer, (B.S. No. 21577). The Eppley standard reference cell, (1.01891 v. at 25°), was kept constantly immersed in a separate oil-bath, maintained at $25^\circ \pm 0.01$.

The potential of each single phase amalgam was read against the two-phase reference amalgam at 18°, 25°, and 30°. This reference amalgam is two-phase at or below 25°, but becomes a single phase system at 30°. The potential between this standard reference electrode at 30° and an amalgam which is still two-phase at that temperature was determined

It was found that the concentrated amalgams at a given temperature give a constant potential indefinitely. The dilute amalgams show a tendency to increase in potential on standing. If, however, the amalgam is thoroughly mixed, it is possible to obtain potential readings at the three temperatures and then to return to the original temperature without any appreciable change in the electromotive force.

While the potentials of the amalgam cells were read at the three temperatures, the values differ so little that, for the sake of brevity, only those for 25° will be given. The values of $-E$ given in Table I represent the mean of many readings taken over a period of from two to ten days. In no case did the readings vary appreciably from the mean value. In this table N_2 is the mol fraction of the zinc in the amalgam, $-E$ is the potential of each individual amalgam against the most dilute amalgam, the values being calculated from the respective values of the potentials measured against the standard two-phase amalgam.

TABLE I
Activity of Zinc in Zinc Amalgams at 25°

| $N \times 10^3$ | - E mv. | $-\frac{E}{0.02958 - \ln N_2}$ | $\frac{a_2}{N_2}$ | $a_2 \times 10^3$ |
|-----------------|------------|--------------------------------|-------------------|-------------------|
| 0.0000 | ∞ | [3.51990] | 1.000 | 0.00 |
| 0.3024 | 0.000 | 3.51942 | 0.9989 | 0.302 |
| 1.5853 | 21.195 | 3.15642 | 0.992 | 1.57 |
| 3.024 | 29.421 | 3.51404 | 0.987 | 2.98 |
| 5.382 | 36.700 | 3.50976 | 0.977 | 5.26 |
| 18.187 | 51.656 | 3.48656 | 0.926 | 16.84 |
| 20.965 | 53.392 | 3.48350 | 0.919 | 19.28 |
| 23.704 | 54.768 | 3.47670 | 0.905 | 21.46 |
| 30.049 | 57.448 | 3.46429 | 0.880 | 26.44 |
| 32.954 | 58.467 | 3.45866 | 0.868 | 28.62 |
| 35.543 | 59.280 | 3.45330 | 0.858 | 30.49 |
| 38.510 | 60.180 | 3.44891 | 0.849 | 32.70 |
| 39.937 | 60.528 | 3.44487 | 0.841 | 33.60 |
| 43.495 | 61.393 | 3.43705 | 0.826 | 35.94 |
| 47.783 | 62.377 | 3.42948 | 0.812 | 38.80 |
| 52.721 | 63.391 | 3.42105 | 0.796 | 41.99 |
| 55.194 | 63.789 | 3.41460 | 0.785 | 43.31 |
| 57.737 | 64.204 | 3.40906 | 0.775 | 44.73 |
| 60.200 | 64.630 | 3.40532 | 0.768 | 46.24 |
| 63.780 | 65.160 | 3.39816 | 0.755 | 48.19 |

The activity of the zinc in the amalgams and the potentials, as well as the increase in free energy accompanying the cell process, are related by the well known thermodynamical expression,

$$\Delta F = E \cdot n \cdot f = RT \ln \frac{a_2}{a_2'} \quad (5)$$

In this the values taken for the constants are: $f = 96494$ coulombs; $R = 8.316$ joules, and $n = 2$.

By rearranging (5), substituting the proper numerical values, and subtracting $\log N_2$ from both sides of the equation, we obtain

$$\log \frac{a_2}{N_2} = \left(\frac{-E}{0.0009922} \cdot \frac{1}{T} - \log N_2 \right) + \log a_2' \quad (6)$$

At infinite dilution, or when a_2/N_2 becomes equal to unity, the left hand member of (6) becomes zero, hence

$$-\log a_2' = \left[\frac{-E}{0.0009922} \cdot \frac{1}{T} - \log N_2 \right] \quad (7)$$

If now we plot the values of the quantity in the brackets, as ordinates, against the mol fractions of zinc, as abscissae, the value of the ordinate where the curve cuts the vertical axis is equal to $-\log a_2'$. We have plotted these values

for the three temperatures and the curves are given in Fig. 3. The value for $-\log a'_2$ for 25° , at infinite dilution, is given in brackets at the top of the third column of Table I. By subtracting this value from the values of the ordinates at other values of N_2 , we have obtained the corresponding values of $\log a_2/N_2$. From these we have calculated the values of a_2/N_2 and a_2 found in the last two columns of this table. From the nature of the method used, it is

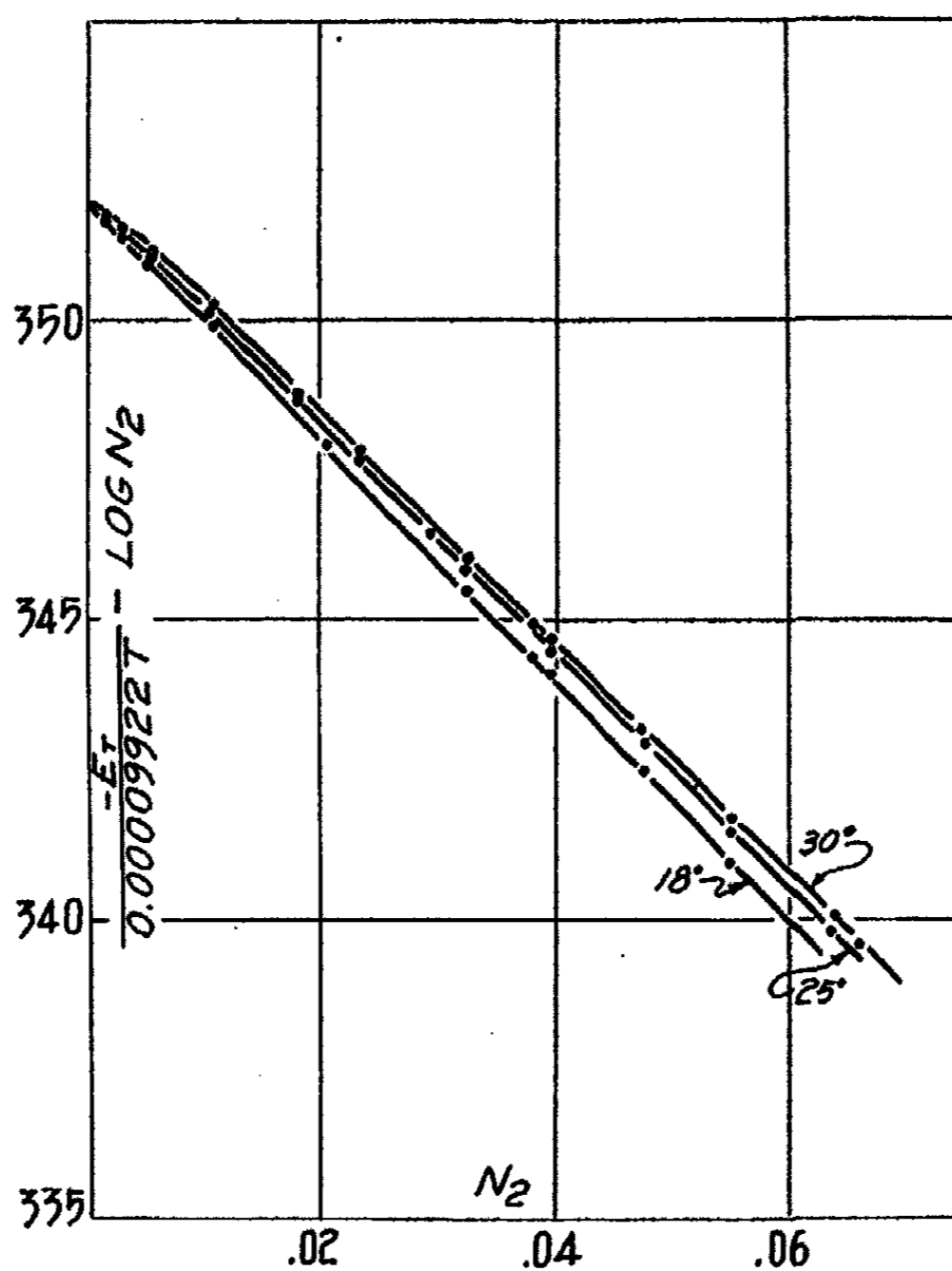


FIG. 3

obvious that the three curves of Fig. 3 must cross at a point corresponding to the most dilute amalgam. The nearer this point is to the vertical axis the less will be the inaccuracy introduced by extrapolation to the axis.

In passing, it is interesting to compare the activities which we have obtained for zinc with those which Lewis and Randall¹ have calculated for thallium from the data of Richards and Daniels.² They have found that the values of a_2/N_2 increases continuously with increasing concentration of thallium in the amalgam. With zinc amalgams, however, exactly the reverse is

¹ Lewis and Randall: "Thermodynamics," 267 (1923).

² Richards and Daniels: J. Am. Chem. Soc., 41, 1732 (1919).

true. The values of a_2/N_2 decrease as the concentration of the zinc is increased. This is precisely what we should expect, if the dissolved zinc is associated in the amalgam.

The variation of the activity of the two components of a binary mixture with change in concentration at a given temperature is given by the relation,

$$\log \frac{a_1}{N_1} = - \int_0^{N_2} \frac{N_2}{N_1} d \log \frac{a_2}{N_2}. \quad (8)$$

To determine the value of the $\log a_1/N_1$ for mercury at any concentration of zinc it is only necessary to plot the values of N_2/N_1 as ordinates against the corresponding values of $\log a_2/N_2$. The area under the curve from the origin, where $N_2 = 0$, up to the desired concentration N_2 gives directly the value of $\log a_1/N_1$ for the desired concentration. We have carefully plotted our values of N_2/N_1 against the corresponding values of $\log a_2/N_2$, and we have repeatedly measured the areas by means of a polar planimeter. The values for a_1/N_1 and a_1 for mercury thus calculated are given in the last two columns of Table II.

TABLE II
Activity of Mercury in Zinc Amalgams at 25°

| $N_2 \times 10^3$ | $N_2/N_1 \times 10^3$ | a_2/N_2 | a_1 |
|-------------------|-----------------------|-----------|--------|
| 0.0000 | 0.0000 | 0.000 | 1.000 |
| 0.3024 | 0.3025 | 0.999 | 0.999+ |
| 1.5853 | 1.5878 | 0.992 | 0.998 |
| 3.024 | 3.033 | 0.987 | 0.997 |
| 5.382 | 5.411 | 0.977 | 0.995 |
| 18.187 | 18.524 | 0.926 | 0.983 |
| 20.965 | 21.414 | 0.920 | 0.980 |
| 23.704 | 24.280 | 0.905 | 0.977 |
| 30.049 | 30.980 | 0.880 | 0.972 |
| 32.954 | 34.077 | 0.869 | 0.969 |
| 35.543 | 36.853 | 0.858 | 0.967 |
| 38.510 | 40.052 | 0.849 | 0.965 |
| 39.937 | 41.598 | 0.841 | 0.964 |
| 43.495 | 45.473 | 0.826 | 0.961 |
| 47.783 | 50.181 | 0.812 | 0.957 |
| 52.721 | 55.655 | 0.796 | 0.953 |
| 55.194 | 58.418 | 0.785 | 0.951 |
| 57.737 | 61.275 | 0.775 | 0.950 |
| 60.200 | 64.056 | 0.768 | 0.948 |
| 63.780 | 68.125 | 0.756 | 0.945 |

In order to determine the effect of temperature upon the electromotive forces of these amalgam cells, we made three sets of cells, one for each temperature, and each set containing exactly the same series of concentrations. These amalgams were prepared in a special pipette which enabled us to weigh

both the zinc and the mercury without mixing. After the pipette had been washed by a stream of pure dry hydrogen and evacuated, the mercury and zinc were mixed and thoroughly shaken. The cells were then sealed and placed in their respective temperature baths. The potentials were read over a period of several days, or until the potentials became constant. From the values of the electromotive forces thus obtained we have calculated the increase in free energy, $-\Delta F$, accompanying the dilution from the more concentrated amalgams, respectively, to the one most dilute. These values for the three temperatures are given in Table III.

TABLE III
Thermodynamic Data for Zinc Amalgam Cells

| $N_2 \times 10^3$ | $-\Delta F_{15}$ joules. | $-\Delta F_{25}$ joules. | $-\Delta F_{30}$ joules. | $\alpha \times 10^4$ | $\beta \times 10^4$ | ΔH_{25} joules. | ΔS_{25} joules. |
|-------------------|-----------------------------|-----------------------------|-----------------------------|----------------------|---------------------|----------------------------|----------------------------|
| 0.0324 | 0000 | 0000 | 0000 | — | — | 0000 | 0000 |
| 1.5853 | 3996 | 4090 | 4165 | 35.09 | +0.323 | 255.2 | 14.58 |
| 3.024 | 5543 | 5678 | 5781 | 35.24 | +0.199 | 354.3 | 20.24 |
| 5.382 | 6912 | 7083 | 7212 | 35.61 | +0.160 | 441.9 | 25.24 |
| 20.965 | 10036 | 10304 | 10475 | 34.80 | -0.338 | 642.9 | 36.72 |
| 32.954 | 10993 | 11283 | 11478 | 35.45 | -0.186 | 703.9 | 40.21 |
| 38.510 | 11310 | 11614 | 11812 | 35.45 | -0.284 | 724.6 | 41.39 |
| 39.937 | 11381 | 11681 | 11836 | 35.72 | -0.140 | 728.8 | 41.63 |
| 47.783 | 11725 | 12038 | 12251 | 36.11 | -0.155 | 751.1 | 42.90 |
| 55.194 | 11989 | 12311 | 12530 | 36.31 | -0.139 | 768.1 | 43.88 |
| Mean | | | | +35.65 | | | |

The temperature coefficients of the electromotive force, and likewise of the change in free energy, were calculated from the potentials at the three temperatures by means of the equation,

$$E_t = E_{25} [1 + \alpha(t - 25) + \beta(t - 25)^2]. \quad (9)$$

These values are also included in Table III.

When the values of β are negligible, as they are for these cells, we may calculate the change in heat content, ΔH , accompanying the dilution from the known value of the free energy of dilution by means of the relation,

$$-\Delta H_{298} = -\Delta F_{298}(1 - \alpha.298). \quad (10)$$

Furthermore, the change in entropy accompanying the dilution is given by the well known relation,

$$-\Delta S = \frac{\Delta F - \Delta H}{T}. \quad (11)$$

The values of ΔH_{298} and ΔS_{298} have been calculated and are to be found in the last two columns of Table III.

For purposes of discussion and comparison, Table IV has been arranged. In this Table E_o represents the observed potentials, E_i the ideal potentials

as calculated by (4), and E_o are the potentials calculated by (3). In these calculations $N_1 = 3305.9$, and N_2 is the mol ratio in the amalgam taken in conjunction with it. In the recalculation of the data of Richards and Forbes, Hildebrand has assumed the value $A = 11.6$. We have found, however, that the value, $A = 11.2$, when substituted in (3), gives better agreement with the observed values not only for the data of Richards and Forbes, but also for our own as well.

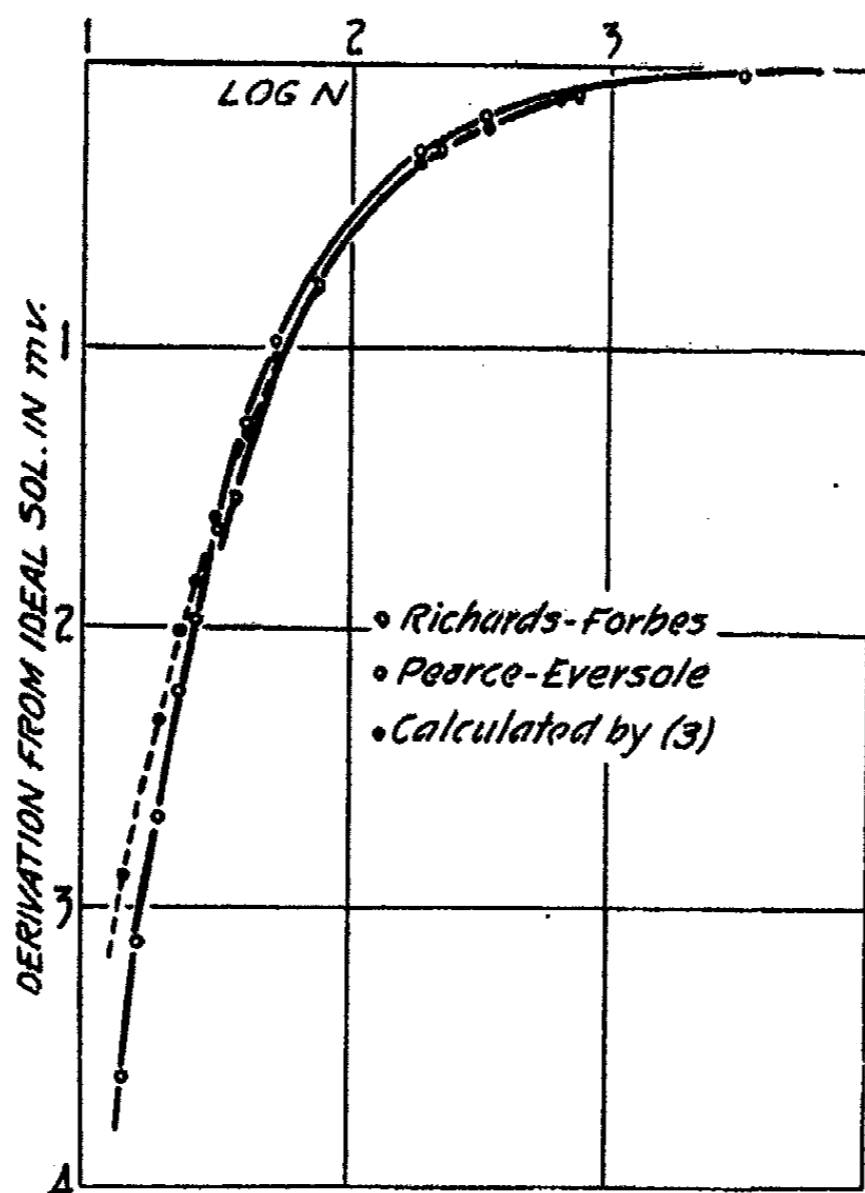


FIG. 4

While the differences between the observed potentials, E_o , and the ideal, E_i , do decrease with increasing dilution of the variable amalgam, N_2 , this difference does persist even at the lowest concentrations. To calculate this deviation for the most dilute amalgam, where $N_1 = 3305.9$, we have calculated the values of E_o and E_i by means of (3) and (4), respectively, and taking N_2 so large that A becomes negligible in comparison. For this purpose we have arbitrarily assumed N_2 to be 100000, and that the resulting amalgam is so dilute that its potential is that of an ideal amalgam. Hildebrand used a similar method in calculating the electromotive force of the most dilute amalgam employed by Richards and Forbes. We have found the deviation for the amalgam, $N = 3305.9$, to be 0.020 mv. This value added to the original deviations gives the corrected deviations which are collected in column, ($E_o -$

E_1), of Table IV. The results show a very close agreement between observed and calculated potential values in the dilute range of concentration, but these values do diverge as we pass to higher concentrations of zinc. The deviations are best shown in Fig. 4. The curves show at once the close agreement between our data and those obtained by Richards and Forbes throughout the concentration range which they studied. They show also that Hildebrand's equation (3) applies with considerable accuracy through a large part of the concentration range which we have studied.

TABLE IV

Deviations of Zinc Amalgams from Ideal Solutions at 25°

| $N_2 \times 10^2$ | N_2/N_1 | E_0 obs. mv. | E_0 calc. mv. | E_1 ideal mv. | $E_0 - E_1$ mv. | $E_0 - E_0$ mv. |
|-------------------|-----------|----------------------|-----------------------|-----------------------|--------------------|--------------------|
| 0.3024 | 3305.90 | 0.000 | 0.000 | 0.000 | -[0.020] | 0.000 |
| 1.5853 | 629.80 | 21.195 | 21.199 | 21.281 | -0.106 | -0.004 |
| 3.024 | 329.70 | 29.421 | 29.403 | 29.576 | -0.175 | +0.018 |
| 5.382 | 184.80 | 36.700 | 36.664 | 36.981 | -0.301 | +0.036 |
| 18.187 | 53.98 | 51.656 | 51.599 | 52.620 | -0.984 | +0.057 |
| 20.965 | 46.70 | 53.392 | 53.285 | 54.451 | -1.079 | +0.102 |
| 23.704 | 41.19 | 54.768 | 54.729 | 56.022 | -1.274 | +0.039 |
| 30.049 | 32.28 | 57.448 | 57.485 | 59.076 | -1.648 | -0.037 |
| 32.954 | 29.35 | 58.467 | 58.452 | 60.252 | -1.805 | -0.075 |
| 35.543 | 27.13 | 59.280 | 59.408 | 61.231 | -1.971 | -0.128 |
| 38.510 | 24.97 | 60.180 | 60.312 | 62.257 | -2.097 | -0.132 |
| 39.937 | 24.04 | 60.528 | 60.723 | 62.726 | -2.218 | -0.195 |
| 43.495 | 21.99 | 61.393 | 61.680 | 63.823 | -2.450 | -0.287 |
| 47.783 | 19.928 | 62.397 | 62.724 | 65.029 | -2.672 | -0.347 |
| 52.721 | 17.968 | 63.391 | 63.807 | 66.292 | -2.921 | -0.416 |
| 55.194 | 17.118 | 63.789 | 64.308 | 66.881 | -3.112 | -0.519 |
| 57.737 | 16.320 | 64.204 | 64.799 | 67.459 | -3.275 | -0.595 |
| 60.200 | 15.611 | 64.630 | 65.253 | 67.998 | -3.388 | -0.623 |
| 63.780 | 14.679 | 65.160 | 65.876 | 68.740 | -3.600 | -0.716 |

Reference should again be made to Fig. 1. In this are shown for comparison the plots of the deviations of the electromotive forces from the data of Richards and Forbes and from that of Hulett and Crenshaw. As stated before, the latter have found that the amalgams behave as ideal solutions up to the concentration at which $\log N = 2.51$. At this point the observed potentials begin to deviate from those calculated for ideal amalgams. Although we have repeated their work, using essentially their method throughout, we have been unable to duplicate their results. On the contrary, our results do confirm those of Richards and Forbes. We have shown that, throughout the whole range of concentration up to saturation, the deviations between the observed and ideal potentials increase regularly as we pass to higher concentrations of zinc. These deviations, on the other hand, approach zero at infinite dilution.

Summary

1. The electromotive forces of zinc amalgam concentration cells have been measured at 18°, 25° and 30°. The amalgam concentrations range from $N = 0.0003024$ up to saturation.
2. The change in free energy, heat content and entropy accompanying dilution have been computed.
3. The activities of the zinc and mercury in the various amalgams have been calculated.
4. The deviation between the observed and ideal potentials increases continuously with increase in the concentration of the zinc. It approaches zero at infinite dilution.
5. The results obtained confirm the work of Richards and Forbes.

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THE BEHAVIOR OF METHANOL OVER ALUMINUM AND ZINC OXIDES*

BY HOMER ADKINS AND PHILIP D. PERKINS

A number of recent publications upon the formation of diethyl ether over oxide catalysts makes it seem advisable to submit some results obtained in 1924 upon the behavior of methanol over aluminum and zinc oxides. The experimental method was essentially the same as that previously described in the study of the dehydration and dehydrogenation of the higher alcohols.¹ That is, about 50 cc. of methanol per hour was passed over a gram of the catalyst heated in a Pyrex tube to 300 to 400°C. The reaction products were passed thru a condenser, then bubbled thru 10 cc. of concentrated sulfuric in each of two 8" \times 1- $\frac{1}{8}$ " test tubes and the undissolved gas collected and measured. The dimethyl ether in the condensate was boiled out at the end of an hour's run, collected in the sulfuric acid and then liberated, collected and measured over water. The ether was liberated by diluting the acid with water to about four times its volume and heating to boiling for a few minutes. The recovery of ether² is at least 99%. The catalysts were of the same sample as those previously used³ and had been used for an hour or two before each of the runs reported, so that their activity had become rather constant. Two thermocouples were used, the head of one being in the catalysts mass, and that of the other outside of the tube but in an indentation adjacent to the catalyst. The dehydration of methanol is a strongly exothermic reaction, so that the difference in temperature indicated by the thermocouples was in some cases as much as 45°.

The variation in the reaction with temperature is shown in Fig. 1. Curve 3 represents the total activity in liters of gas per hour and curve 4 the activity in liters of dimethyl ether per hour. The temperature shown is that of the inside thermocouple. Curves 1 and 2 show the same values for activities plotted against the temperature as indicated by the outside thermocouple. It is apparent from the curves that methanol is converted almost quantitatively over the alumina catalyst used into dimethyl ether in increasing amounts at temperatures up to about 350° and that there is little change in either activity or proportions of products over a range of perhaps 40°. Further increase of temperature results in a rapid increase in the products other than dimethyl ether (CO₂, CO, C₂H₄, H₂, and CH₄) partly at the expense of that compound.

The behavior of methanol over a zinc oxide catalyst is shown in Fig. 2, the temperature being that of a thermocouple in the catalyst mass. The forma-

*Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin.

¹ Adkins and Perkins: J. Am. Chem. Soc., 47, 1163 (1925).

² McKee and Burke: J. Ind. Eng. Chem., 15, 793 (1923).

³ Adkins and Perkins: J. Am. Chem. Soc., 47, 1163; Lazier and Adkins: 1719 (1925).

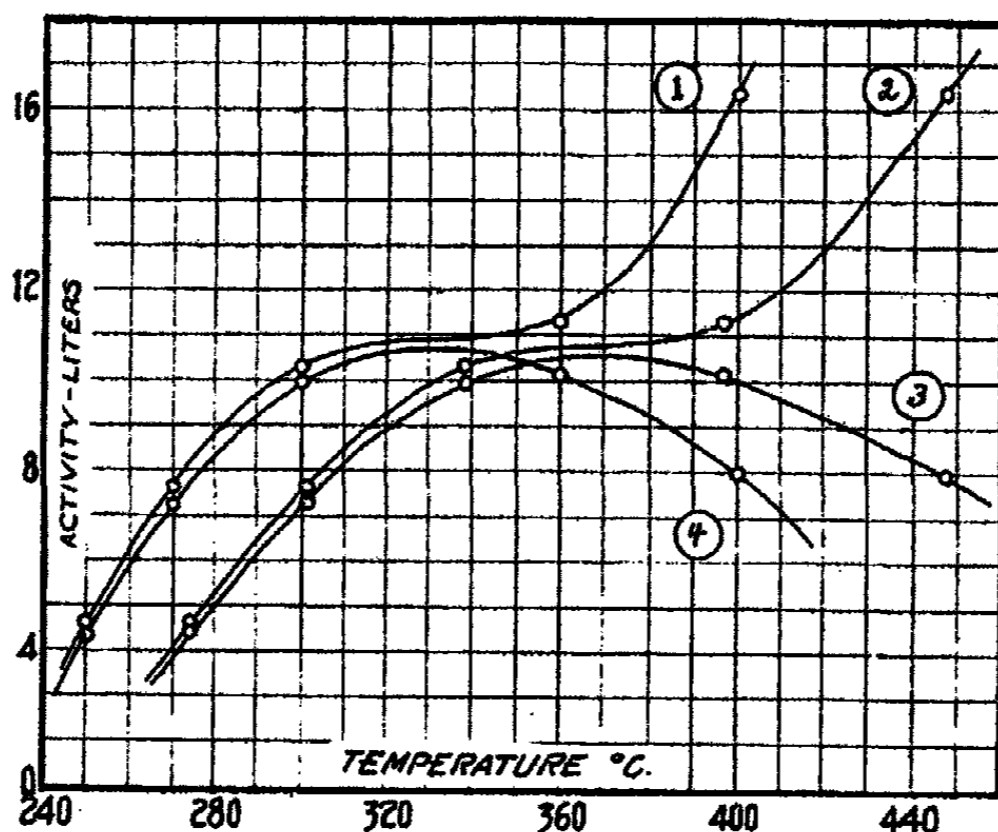


FIG. 1
Methanol over Alumina

The liters of gas at 22° and 740 mm formed per hour by the passage of 50 cc of methanol over 1 g. of alumina, are plotted against the temperatures indicated by a thermocouple outside the catalyst tube (curve 1) and in the catalyst mass (curve 2). The liters of dimethyl ether contained in the gas are similarly shown in curves 3 and 4.

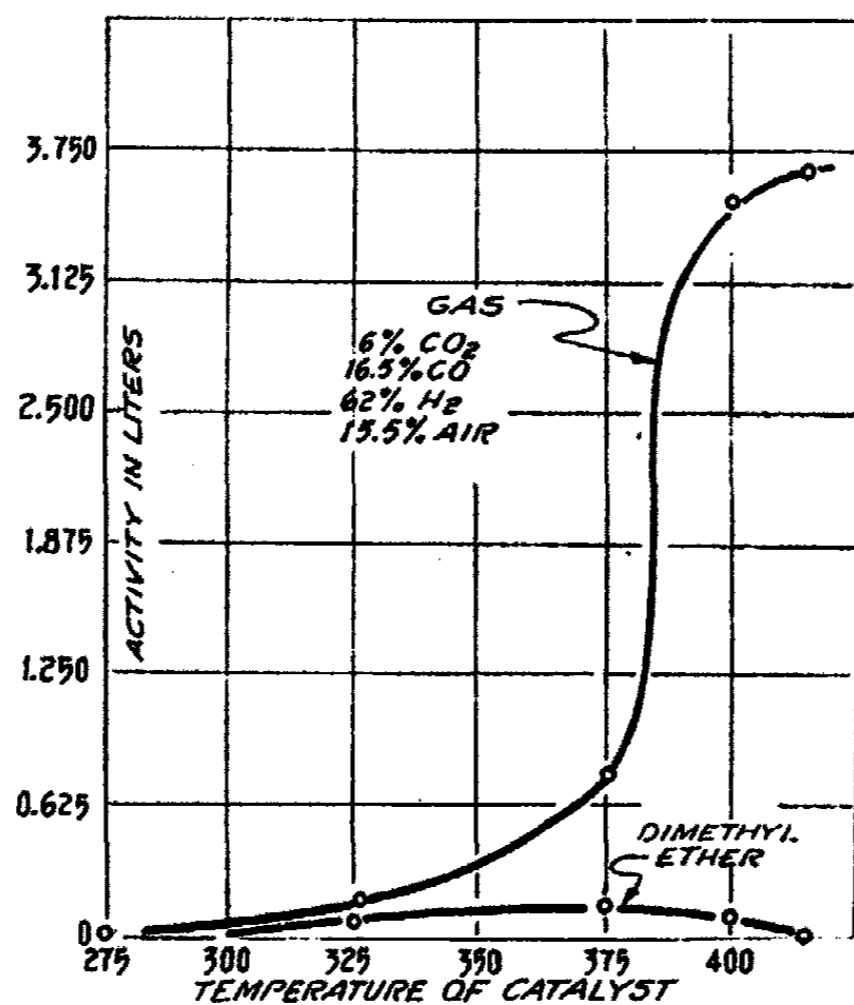


FIG. 2
Methanol over Zinc Oxide

The liters of gas and dimethyl ether at 20° and 740 mm, formed per hour by the passage of 50 cc of methanol over 1 g. of precipitated zinc oxide, are plotted against the temperature indicated by a thermocouple in the catalyst mass. A representative gas analysis is shown in the figure.

tion of dimethyl ether was almost negligible over this catalyst. The formation of simple gaseous products became prominent at about the same temperature as in the case of alumina. There was a considerable amount of blackening of the catalyst.

A series of experiments were conducted in which dimethyl ether was passed over the alumina catalyst along with varying amounts of water at temperatures from 270° to 430°. Six to nine liters per hour of dimethyl ether was passed over the catalyst. The results of a number of runs are given in Fig. 3, showing the variation with temperature of the amount of dimethyl ether

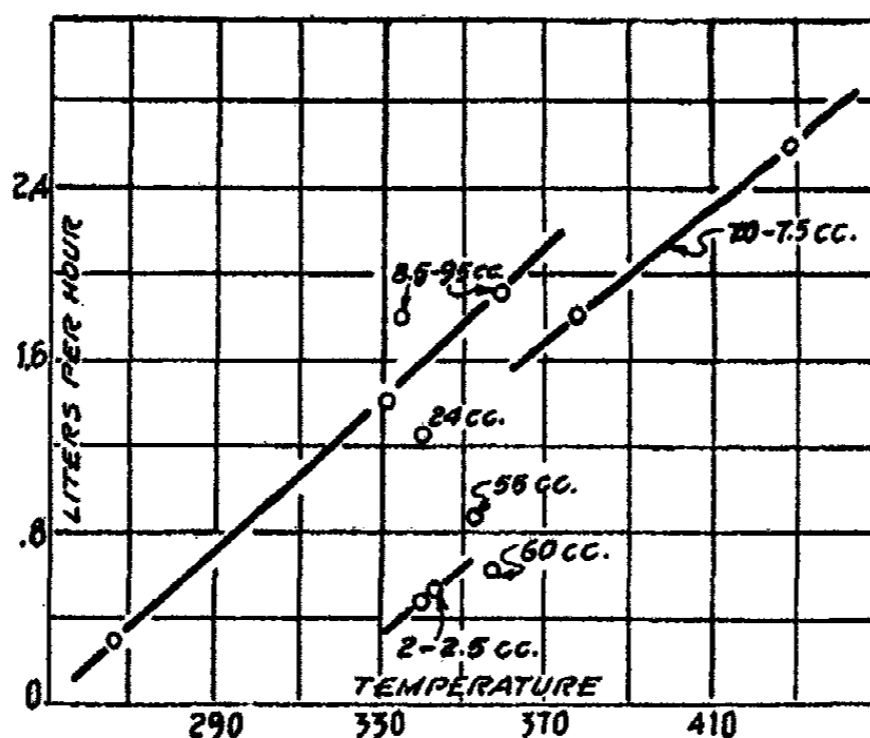


FIG. 3
Hydration of Dimethyl Ether

The liters of dimethyl ether hydrated at various temperatures using various amounts of water with a flow of approximately seven liters of the ether per hour over 1 g. of an alumina catalyst are shown.

entering into reaction with varying amounts of water. It is apparent that the greatest amount of hydration took place when 8 to 10 cc. of water per hour was used. This corresponds to a 50% molecular excess of water, greater or lesser amounts of water decreasing the reaction. These results were obtained using 1 g. of alumina catalyst. When 6 g. of catalyst was used the maximum reaction was obtained with about 60 g. of water, i.e. 700% molecular excess per hour. The actual amount of ether hydrated per hour was approximately twice the amount hydrated over 1 g. of catalyst.

The water for the hydration was passed into the vaporizer in the same fashion as the alcohol in the dehydration experiments. The dimethyl ether was passed from a bottle under a light pressure and mixed with the steam just after it left the vaporizer. The amount of dimethyl ether reacting was determined by subtracting from the amount introduced the amount found in the gas, collected as in the dehydration experiments. As a check on this method the amount of methanol in the distillate was determined by the use of a Zeiss immersion refractometer. In general this showed 75 to 80% as much methanol as corresponded to the dimethyl ether disappearing.

Dimethyl ether was prepared in quantity by passing methanol over alumina at 340° , passing the products thru a condenser and receiver surrounded by ice water, and then absorbing the gas in conc. sulfuric acid. 100 cc. of sulfuric acid will satisfactorily absorb the ether until the volume is 400 cc. The slightly brown solution may be kept at room temperature and pressure. A water-white solution may be obtained by carrying out the absorption at 0° . When a supply of 10 or 12 liters of the ether was needed, 30 cc. of the solution in acid was placed in a $8\frac{1}{2}'' \times 1\frac{1}{8}''$ test tube and water slowly added until the tube was three fourths full. The evolved gas was collected over water. About 50% of the dissolved ether is liberated during the addition of the water and the remainder upon heating the solution to boiling in an oil bath for a few minutes.

Summary and Conclusions

The relation of temperature to the rate of dehydration of methanol over an alumina catalyst has been shown. There is a very small amount of decomposition of the ether between 350° - 380° . Decomposition increases rapidly above that point.

Zinc oxide precipitated as the hydroxide is very inactive towards methanol at 325° and induces a negligible ether formation at any temperature. At temperatures above 325° zinc oxide shows a rapidly increasing tendency to decompose methanol.

The optimum concentration of water for maximum hydration of dimethyl ether at a constant rate of flow is shown to vary with the amount of catalyst.

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STUDIES IN HOMOGENEOUS GAS REACTIONS I

BY LOUIS STEVENSON KASSEL

Introduction

During the last few years the theory of activation by collision, rather than by radiation, has made rapid strides. Subsequent to the suggestion of activation by radiation by Perrin,¹ Lindemann² showed that on the basis of the simple radiation hypothesis the inversion of sucrose must be enormously accelerated by sunlight, in disagreement with experiment. Many other cases are now known in which the frequency which is calculated from the simple radiation hypothesis is quite without effect on a system; frequently it falls in a region in the infra-red which is not absorbed at all. At about the same time, Langmuir³ pointed out that there is not enough radiant energy in a system to account for the observed rates of reaction. Also, Lindemann⁴ called attention to the fact that, if the rates of activation and de-activation are large compared to the rate of reaction, the reaction may be kinetically unimolecular regardless of the order of the activation process. Calculations have been made by Christiansen and Kramers,⁵ by G. N. Lewis,⁶ and by Tolman⁷ which deal with the maximum possible rates of activation by radiation and by collision. In all of these calculations it was found necessary to make rather undesirably liberal assumptions to account for the observed rates of reaction; it cannot be said that they were very favorable to either method of activation.

Since these last-mentioned calculations were published, two distinct arguments in favor of activation by collision have appeared. The first of these is of an experimental nature; Hinshelwood and his co-workers⁸ have found that the decompositions of propaldehyde, of diethyl ether, and of dimethyl ether, all of which are strictly unimolecular at high pressures, deviate from the unimolecular course at low pressures, the specific reaction rate becoming smaller with decreasing pressure; Ramsperger⁹ has observed the same type of decrease in the specific rate in the decomposition of azomethane, and to a greater extent than in any of the cases studied by Hinshelwood. This decrease in the specific rate with decreasing pressure removes the very feature of unimolecular reactions which the radiation hypothesis was invented to explain,

¹ "Les Atomes" (1913); *Ann. Phys.*, **11**, 5 (1919).

² *Phil. Mag.*, **40**, 871 (1920).

³ *J. Am. Chem. Soc.*, **42**, 2190 (1920).

⁴ *Trans. Faraday Soc.*, **17**, 598 (1922).

⁵ *Z. physik. Chem.*, **104**, 451 (1923).

⁶ Lewis and Smith: *J. Am. Chem. Soc.*, **47**, 1508 (1925).

⁷ *J. Am. Chem. Soc.*, **47**, 1524 (1925).

⁸ Hinshelwood and Thompson: *Proc. Roy Soc.*, **113A**, 221 (1926); Hinshelwood: **114A**, 84, (1927); Hinshelwood and Askey: **115A**, 215 (1927).

⁹ *J. Am. Chem. Soc.*, **49**, 912, 1495 (1927).

and may be regarded as experimental evidence that radiation alone is not sufficient to cause the thermal decompositions of the above-mentioned substances. The second of these arguments in favor of activation by collision is based upon the suggestion made by Christiansen¹⁰ that the number of degrees of freedom of the molecule must be considered. This idea has been the basis for calculations by Hinshelwood¹¹ and by Fowler and Rideal¹² which show that the maximum rate of activation is very much increased by this assumption. In the paper by Fowler and Rideal there are some other assumptions made as to the method of activation which seem rather questionable, and which have been criticized by Tolman, Yost, and Dickinson.¹³ The treatment given by Hinshelwood seems to be preferable, and will be discussed in a later section. It may be said that as a result of this treatment it proves possible to account fairly well for the experimental results of Hinshelwood himself, but that the much faster decompositions of azomethane and of nitrogen pentoxide would require the assumption of an absurd number of degrees of freedom. Hinshelwood assumed that the specific reaction rate of all activated molecules was a constant, independent of their energy content. In this paper the consequences of replacing this assumption by the more reasonable one that the specific reaction rate for active molecules increases with their energy content will be considered. Just before the paper was submitted, an article appeared by Rice and Ramsperger¹⁴ in which this same assumption was made. The development and the final result are in many respects similar to that presented here, but there are enough differences to make publication of this article seem desirable.

The Energy of Activation

There seems to be some disagreement in the literature about the meaning to be given to the energy of activation. In the original Arrhenius equation,

$$\frac{d \ln K}{dT} = \frac{q}{RT^2},$$

q is the energy per mol necessary for activation, that is, the difference between the average energy of the activated molecules and the average energy of all the molecules. Tolman¹⁵ as the result of a rigorous and very general derivation, has obtained the expression

$$\frac{d \ln K}{dT} = \frac{\bar{E} - \bar{E}}{kT^2},$$

¹⁰ Proc. Camb. Phil. Soc., 23, 438 (1926).

¹¹ Proc. Roy. Soc., 113A, 230 (1926).

¹² Proc. Roy. Soc., 113A, 570 (1926).

¹³ Proc. Nat. Acad. Sci., 13, 188 (1927).

¹⁴ J. Am. Chem. Soc., 49, 1617 (1927).

¹⁵ J. Am. Chem. Soc., 47, 2652 (1925); "Statistical Mechanics," 265 (1927).

where \bar{E} is the average energy of the molecules that react and \bar{E} is the average energy of all the molecules; this equation applies to unimolecular reactions in which the equilibrium quota of activated molecules is essentially maintained; for other cases, Tolman's paper must be consulted. Tolman, then, proposes to call this quantity $\bar{E} - \bar{E}$ the energy of activation. Lewis,¹⁶ on the other hand, defines the energy of activation as the minimum internal energy that a molecule must have in order to react; this definition does not involve any equation. This definition seems preferable to that of Tolman, because many simple hypotheses as to the nature of the activated states give values of $\bar{E} - \bar{E}$ which are not constant with respect to the temperature; it should certainly be a fundamental requirement for any definition of the energy of activation that it be independent of the temperature.

Thus, for the simple case characterized by two internal degrees of freedom for the molecule, and maintenance of the equilibrium quota of activated molecules, Lewis¹⁷ has calculated the temperature coefficient of the reaction rate, assuming, (a), that the specific reaction rate of activated molecules is independent of their energy content, and, (b), that the specific reaction rate is proportional to the excess energy over some critical amount, E_0 . Assumption (a) leads to the equation

$$\frac{d \ln K}{dT} = \frac{E_0}{kT^2},$$

while (b) gives

$$\frac{d \ln K}{dT} = \frac{E_0 + kT}{kT^2}.$$

These same results might have been obtained directly from Tolman's equation. Thus for the first case

$$\bar{E} = \frac{\int_{E_0}^{\infty} N k T e^{-E/kT} E dE}{\int_{E_0}^{\infty} N k T e^{-E/kT} dE} = E_0 + kT,$$

and

$$\bar{E} = \frac{\int_0^{\infty} N k T e^{-E/kT} E dE}{\int_0^{\infty} N k T e^{-E/kT} dE} = kT$$

¹⁶ Lewis and Smith: J. Am. Chem. Soc., 47, 1512 (1925).

¹⁷ Lewis and Smith: J. Am. Chem. Soc., 47, 1513 (1925).

Whence

$$\frac{d \ln K}{dT} = \frac{\bar{E} - \bar{E}}{kT^2} = \frac{E_0}{kT^2},$$

just as Lewis found. And in the second case

$$\bar{E} = \frac{\int_{E_0}^{\infty} e^{-E/kT} (E - E_0) E dE}{\int_{E_0}^{\infty} e^{-E/kT} (E - E_0) EdE} = E_0 + 2 k T$$

and \bar{E} is the same as before. Therefore

$$\frac{d \ln K}{dT} = \frac{E_0 + k T}{kT^2}.$$

Thus we see that assumption (a) corresponds to a type of reaction in which Tolman's definition of the energy of activation is the same as Lewis's, but that assumption (b) corresponds to a type in which the energy of activation as defined by Tolman is not only larger than that given by Lewis, but is variable, increasing with temperature.

Since many other examples could be given in which this same sort of variation would occur, it seems best to adopt the definition given by Lewis. Accordingly, in this paper, the energy of activation is defined as the minimum internal energy per mol which molecules must attain in order to react. This same definition has been adopted by Rice and Ramsperger also.

The Specific Reaction Rate of Activated Molecules

The paper of Rice and Ramsperger dealt almost entirely with two theories; that which they have called Theory I, which is simply the theory considered by Hinshelwood, and Theory II, in which it is assumed that an activated molecule does not react until some particular degree of freedom acquires energy of E_0 or greater. On the basis of this assumption it is possible to calculate, from statistical mechanics, the way in which the specific reaction rate of activated molecules changes with their energy contents. They have applied these two theories to Hinshelwood and Thompson's results on propaldehyde, and found that the form of the curve obtained by plotting $\log K$ against $\log p$ (at a fixed temperature) is given fairly well by either theory.

The author has also developed Hinshelwood's theory, in much the same way as have Rice and Ramsperger, and obtained the same result. It is found that

$$K = \frac{K_{\infty}}{1 + \beta_1/p}$$

where β_1 is a constant at any fixed temperature; this is equation (5) in Rice and Ramsperger's paper. The author has found it very convenient in testing this theory to plot $1/K$ against $1/p$. According to the equation, this plot must be a straight line, from whose intercepts K_∞ and β_1 may be found at once. It is thus very easy to tell whether the data for any particular reaction

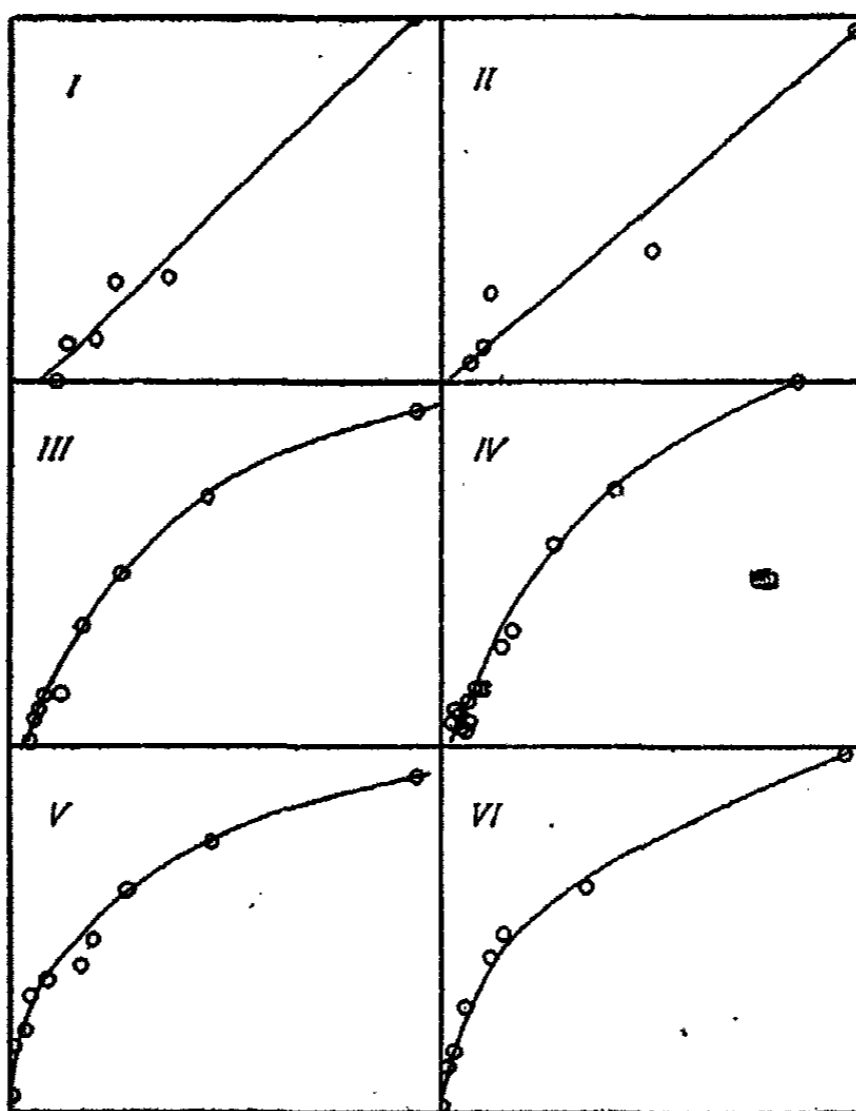


FIG. 1

I Propaldehyde 849°
 III Diethyl Ether 798°
 V Azomethane 603°

II Propaldehyde 796°
 IV Dimethyl Ether 777°
 VI Azomethane 563°

are in agreement with this theory or not. In this way it is found that the experimental data for diethyl ether, dimethyl ether, and azomethane are in definite disagreement with the requirements of the simple theory; propaldehyde gives straight lines within the accuracy of the experimental results. The experimental results for all four of these substances are plotted in Fig. 1.

Thus it seemed that, although the assumption of a reasonable number of degrees of freedom was capable of accounting for the order of magnitude of the reaction rates of most monomolecular reactions, it was not able to account quantitatively for the variation of specific rate with pressure. Also, it was found that the theory was unable to account for even the order of magnitude

in the case of some of the faster reactions, notably the decompositions of azomethane and nitrogen pentoxide, without assuming an unreasonable number of degrees of freedom.

A second theory was then developed, based upon the following argument. In a complex molecule it is not sufficient to have a large amount of energy stored to cause decomposition. It is necessary for this energy, or a sufficient part of it, to be concentrated at some weak point in order to rupture the molecule. Now the simplest possible assumption is that there is some single bond in the molecule which is easier to break than any of the others, and that all but an inappreciable part of the reaction is initiated by a break of this bond. Then, if we assume that the bond breaks whenever it acquires energy in excess of some critical amount, E_0 , it should be possible to calculate from statistical mechanics a relation between the specific reaction rate of activated molecules and their energy content.

This differs from Theory II of Rice and Ramsperger in one way: they assumed that it was necessary for the energy E_0 to be concentrated in a single degree of freedom; the author has regarded a chemical bond as similar to a simple oscillator, and hence possessing two degrees of freedom. Save for the differences resulting directly from this one variation, the two developments are very similar.

Following Rice and Ramsperger, let a molecule of Class A be one whose total internal energy is between E and $E + dE$, and a molecule of Class C be one which is of Class A and in which some particular bond (that is, some particular *two* degrees of freedom) has energy in excess of E_0 . We assume that the rate at which molecules of Class A enter Class C is proportional to the fraction of the molecules of Class A which, *at equilibrium*, would belong to Class C. The assumptions involved in this are very clearly outlined by Rice and Ramsperger on page 1622 of their article, and are exactly the same in this theory as in theirs.

We wish, then, to determine the fraction of all molecules which have energy between E and $E + dE$ and which would have also, if the distribution law held, energy in excess of E_0 in some definite two degrees of freedom.

This calculation may be made in a way analogous to that used by Rice and Ramsperger. It may also be done in a different way, somewhat more elegant mathematically; a similar method is not available for the case treated by Rice and Ramsperger, because of the non-integrability of one of the equations. It is this second method which will be given here.

For a single oscillator it is well known that the probability of energy in the range from E to $E + dE$ is

$$P_{1,E,dE} = \frac{1}{kT} e^{-E/kT} dE,$$

and that the probability of energy greater than E is

$$P_{1,E} = e^{-E/kT}.$$

Then it follows at once that the probability that a system of two oscillators will have energy greater than E is

$$P_{2,E} = \int_0^E \left[\left(\frac{1}{kT} e^{-E_0/kT} dE_0 \right) \left(e^{-\frac{E-E_0}{kT}} \right) \right] + e^{-E/kT}$$

$$= \left(\frac{E}{kT} + 1 \right) e^{-E/kT}$$

In this expression the first term within the brackets is the probability that a chosen one of the oscillators will have energy in the range E_0 to $E_0 + dE_0$ and the second term is the probability that the other will have energy greater than $E - E_0$, so that the two together will have energy greater than E . The integral of this product from $E_0 = 0$ to $E_0 = E$ plus the probability that the first oscillator will have energy greater than E , is evidently the total probability that the two together will have energy greater than E .

It is then easy to find the probability that the two oscillators together will have energy in the range from E to $E + dE$. This is

$$P_{2,E,dE} = - \frac{\partial P_{2,E}}{\partial E} dE$$

$$= \frac{E}{(kT)^2} e^{-E/kT} dE.$$

Continuing in this way, it is found that the probability that S oscillators have energy greater than E is

$$P_{S,E} = \int_0^E \left\{ \left[\frac{1}{kT} e^{-E_0/kT} dE_0 \right] \left[\frac{1}{(S-2)!} \left(\frac{E-E_0}{kT} \right)^{S-2} + \dots + \right. \right.$$

$$\left. \left. \frac{E-E_0}{kT} + 1 \right] e^{-\frac{E-E_0}{kT}} \right\} + e^{-E/kT} \quad (1)$$

$$= \left[\frac{1}{(S-1)!} \left(\frac{E}{kT} \right)^{S-1} + \dots + \frac{1}{1!} \left(\frac{E}{kT} \right) + 1 \right] e^{-E/kT}$$

and the probability that they have energy in the range from E to $E + dE$ is

$$P_{S,E,dE} = - \frac{\partial P_{S,E}}{\partial E} dE$$

$$= \frac{E^{S-1}}{(S-1)! (kT)^S} e^{-E/kT} dE$$

These are of course all well-known results. Evidently the integrand of (1), namely,

$$C_{S,E,E_0,dE_0} = \left[\frac{1}{kT} e^{-E_0/kT} dE_0 \right] \left[\frac{1}{(S-2)!} \left(\frac{E-E_0}{kT} \right)^{S-2} + \dots + \frac{1}{1!} \frac{E-E_0}{kT} + 1 \right] e^{-\frac{E-E_0}{kT}}$$

is the probability that some chosen one of the S oscillators will have energy in the range E_0 to $E_0 + dE_0$ and that the whole group will have energy greater than E . Hence the probability that the whole group will have energy in the range E to $E + dE$ and that the chosen one will have energy in the range E_0 to $E_0 + dE_0$ is given by

$$C_{S,E,dE,E_0,dE_0} = - \frac{\partial C_{S,E,E_0,dE_0}}{\partial E} dE$$

$$= \frac{1}{(S-2)!} \frac{(E-E_0)^{S-2}}{(kT)^S} e^{-E/kT} dE dE_0$$

But it has already been found that the probability that the whole group will have energy in the range from E to $E + dE$ is

$$P_{S,E,dE} = \frac{E^{S-1}}{(S-1)! (kT)^S} e^{-E/kT} dE$$

Hence the probability that when the S oscillators have energy in the range E to $E + dE$ some chosen one of them has energy in the range from E_0 to $E_0 + dE_0$ is

$$C_{S,E,dE,E_0,dE_0}^I = \frac{C_{S,E,dE,E_0,dE_0}}{P_{S,E,dE}} = \frac{(S-1)(E-E_0)^{S-2}}{E^{S-1}} dE_0$$

Then, finally, the probability that when the whole group has energy in the range E to $E + dE$ some chosen one of them has energy greater than E_0 is

$$C_{S,E,E_0}^I = \int_0^E C_{S,E,dE,E_0,dE_0}^I = \left(\frac{E-E_0}{E} \right)^{S-1}$$

Hence the specific reaction rate of molecules with energy E is

$$A \left(\frac{E-E_0}{E} \right)^{S-1}$$

where A is the proportionality constant.

It only remains to evaluate this constant in terms of the rate at high pressures. When the equilibrium quota of activated molecules is maintained, the number of molecules with energy between E and $E + dE$ that decompose per second is

$$NK_E dE = \left[\frac{NE^{S-1}}{(S-1)!(kT)^S} e^{-E/kT} dE \right] \left[A \left(\frac{E - E_0}{E} \right)^{S-1} \right]$$

where N is the total number of molecules. Then the total number of molecules that decompose per second is

$$NK_\infty = \int_{E_0}^{\infty} NK_E dE = N A e^{-E_0/kT}$$

Hence the observed specific reaction rate at high pressures will be

$$K_\infty = A e^{-E_0/kT}$$

That is,

$$A = K_\infty e^{+E_0/kT},$$

and hence the specific reaction rate of activated molecules of energy E is

$$K_\infty e^{E_0/kT} \left(\frac{E - E_0}{E} \right)^{S-1}$$

This is the quantity that Rice and Ramsperger have called b_E ; the corresponding equation in their theory is (18); it is

$$b_E = K_\infty \frac{\Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n+1}{2}\right)} e^{E_0/kT} \left(\frac{E - E_0}{kT} \right)^{\frac{1}{2}} \left(\frac{E - E_0}{E} \right)^{n/2-1}$$

It is of interest to calculate $\bar{\bar{E}}$ and \bar{E} in Tolman's equation

$$\frac{d \ln K}{dT} = \frac{\bar{\bar{E}} - \bar{E}}{kT^2}$$

Evidently

$$\begin{aligned} \bar{\bar{E}} &= \frac{\int_{E_0}^{\infty} (E - E_0)^{S-1} E e^{-E/kT} dE}{\int_{E_0}^{\infty} (E - E_0)^{S-1} e^{-E/kT} dE} \\ &= E_0 + S k T \end{aligned}$$

and

$$\bar{E} = \frac{\int_0^{\infty} E \cdot E^{S-1} e^{-E/kT} dE}{\int_0^{\infty} E^{S-1} e^{-E/kT} dE} = S k T.$$

Hence

$$\bar{E} - E_0 = E_0$$

and

$$\frac{d \ln K}{dT} = \frac{E_0}{kT^2},$$

as could have been seen directly.

Thus if the assumption made by Rice and Ramsperger that reaction occurs whenever some single degree of freedom in the molecule acquires energy in excess of E_0 be replaced by the very similar assumption that reaction occurs whenever some bond (two degrees of freedom) in the molecule acquires energy in excess of E_0 , a slightly simpler, but very similar result is obtained for the specific reaction rate of activated molecules. If it is remembered that S in the present theory is equal to $n/2$ in the notation of Rice and Ramsperger, since the number of degrees of freedom is twice the number of oscillators, it is evident that the difference is in the direction of a relatively greater specific reaction rate for the molecules of high energy in the Rice and Ramsperger theory than in that of the author; this effect, however, is not a large one.

The Rate of Activation of Molecules

The next problem is to find the actual reaction rate when the pressure is not so high that the equilibrium quotas of activated molecules are maintained. If, following Hinshelwood and Rice and Ramsperger, we assume that at all temperatures and pressures the rate of activation is equal to the rate at which activated molecules would participate in collisions if the equilibrium quota of them were present, we may again use part of Rice and Ramsperger's derivation. They have shown that

$$K = \int_{E_0}^{\infty} \frac{W_E b_E dE}{1 + b_E k T / (ap)}$$

where $W_E dE$ is the equilibrium quota of molecules with energy between E and $E + dE$, b_E is the specific reaction rate of these molecules, and

$$a = 4 \sqrt{\frac{\pi k T}{m}} \sigma^2.$$

Here we have

$$W_E = \frac{1}{\Gamma(S) (kT)^S} E^{S-1} e^{-E/kT},$$

and

$$b_E = A \left(\frac{E - E_0}{E} \right)^{S-1}$$

When these substitutions are made, the resulting equation reduces to

$$\frac{K}{K_\infty} = D \int_0^\infty \frac{e^{-x/RT} dx}{\frac{1}{x^{S-1}} + \frac{A/BN}{(x + E_0)^{S-1}}},$$

where $D = \frac{1}{\Gamma(S) (kT)^S}$ and $B = 4 \sqrt{\frac{\pi RT}{M}} \sigma^2$,

a form which is suitable for calculation. It is not possible to perform the integration algebraically, and it is thus necessary to obtain numerical values by graphical means or by quadratures.

Test of the Theory

The data of Ramsperger on the decomposition of azomethane afford the best test of any theory which concerns itself with the decrease of reaction rate with pressure, since the reaction has been studied at pressures low enough to give a very considerable decrease, at two temperatures. This last fact is of great importance, as will be seen.*

The high-pressure measurements on azomethane may be fairly well represented by

$$\log K = 15.96512 - 11180.12/T,$$

or

$$K = 9.228 \times 10^{15} e^{-51130/RT}.$$

Comparison of this with the theoretical equation for high pressures shows that

$$A = 9.228 \times 10^{15},$$

and

$$E_0 = 51130.$$

Here E_0 and R are in calories per gram molecule. If it is assumed that

$$\sigma^2 = 5 \times 10^{-16} \text{ cm}^2$$

then

$$B = 5.214 \times 10^{-11}.$$

Then it only remains to select values for T and S ; for, when this has been done, D may be calculated, and K is thus expressed as a function of N only. The resulting integrals have been found by quadratures for a number of values of S and N . The results are summarized in the following tables.

| S = 6, T = 603 | | | | | | |
|------------------|-------------------|-------------------|-------------------|-------------------|-----------------|--|
| N | 10^{23} | 10^{22} | 10^{21} | 10^{20} | 10^{19} | |
| (P cm) | 6.2×10^6 | 6.2×10^4 | 6.2×10^3 | 6.2×10^2 | 6.2×10 | |
| K/K _∞ | .9162 | .6528 | .3055 | .0937 | .0193 | |

| S = 9, T = 603 | | | | | | |
|------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| N | 10^{21} | 10^{19} | 10^{18} | 10^{17} | 10^{16} | 10^{16} |
| P | 6200 | 62 | 6.2 | .62 | .062 | .0062 |
| K/K _∞ | .7889 | .2091 | .06383 | .01495 | .002905 | .0004537 |

| S = 12, T = 603 | | | | | | |
|------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| N | 10^{20} | 10^{19} | 10^{18} | 10^{17} | 10^{16} | 10^{16} |
| P | 620 | 62 | 6.2 | .62 | .062 | .0062 |
| K/K _∞ | .8614 | .5747 | .3203 | .1008 | .03005 | .006242 |

| S = 12, T = 563 | | | | | | |
|------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| N | 10^{20} | 10^{19} | 10^{18} | 10^{17} | 10^{16} | 10^{16} |
| P | 580 | 58 | 5.8 | .58 | .058 | .0058 |
| K/K _∞ | .9601 | .6847 | .3708 | .1425 | .04158 | .009975 |

In considering these values several points are to be kept in mind. If the value of σ^2 is altered, it is not necessary to recalculate the integrals; new tables may be prepared from the ones given by reducing the values of N and P in the same ratio in which σ^2 has been increased; an inspection of the equation which governs K shows the correctness of this procedure. The values of A and E_0 used in this calculation are those obtained from the measurements in Ramsperger's first paper. It is likely that both A and E_0 are a little too small; the values of K_∞ determined by extrapolation at 603° and 563° are 3.09×10^{-3} and 1.38×10^{-4} as compared with 2.66×10^{-3} and 1.28×10^{-4} as given by the equation. For this reason, in comparing observed and calculated values of the reaction rates, the comparison is made between values of K/K_∞ and not between values of K; when this is done the error caused by inaccurate values of A and E_0 is small.

In Fig. 2 the calculated values of K/K_∞ are compared with the experimental values. Here σ^2 has been taken as 1.5×10^{-14} , and the values of P given in the tables have been corrected accordingly. It is evident that the experimental results are fitted very well by taking $s = 12$, $\sigma^2 = 1.5 \times 10^{-14}$; they could be fitted equally well by a smaller value of s, in conjunction with a larger value for σ^2 . Thus, so far, the theory has proved satisfactory; but the real test is yet to come. It is now possible to calculate the specific reaction rate at any temperature and pressure, all of the arbitrary constants having been chosen. In Fig. 3 the theoretical curve for $T = 563$ is compared with the experimental one; the agreement is little short of remarkable.

Thus Ramsperger's results on the decrease in specific reaction rate with decrease in pressure may be quantitatively explained by taking $\sigma^2 = 1.5 \times$

10^{-14} , $S = 12$. They could be explained about as well, probably, by larger or smaller values of S , with correspondingly changed values of σ^2 . It may be advanced in criticism of this theory that the values chosen for S and σ^2 are both larger than is probable for such a molecule as azomethane. But it must be remembered that an activated molecule has a very high "internal temperature" and that many of the degrees of freedom that are normally frozen

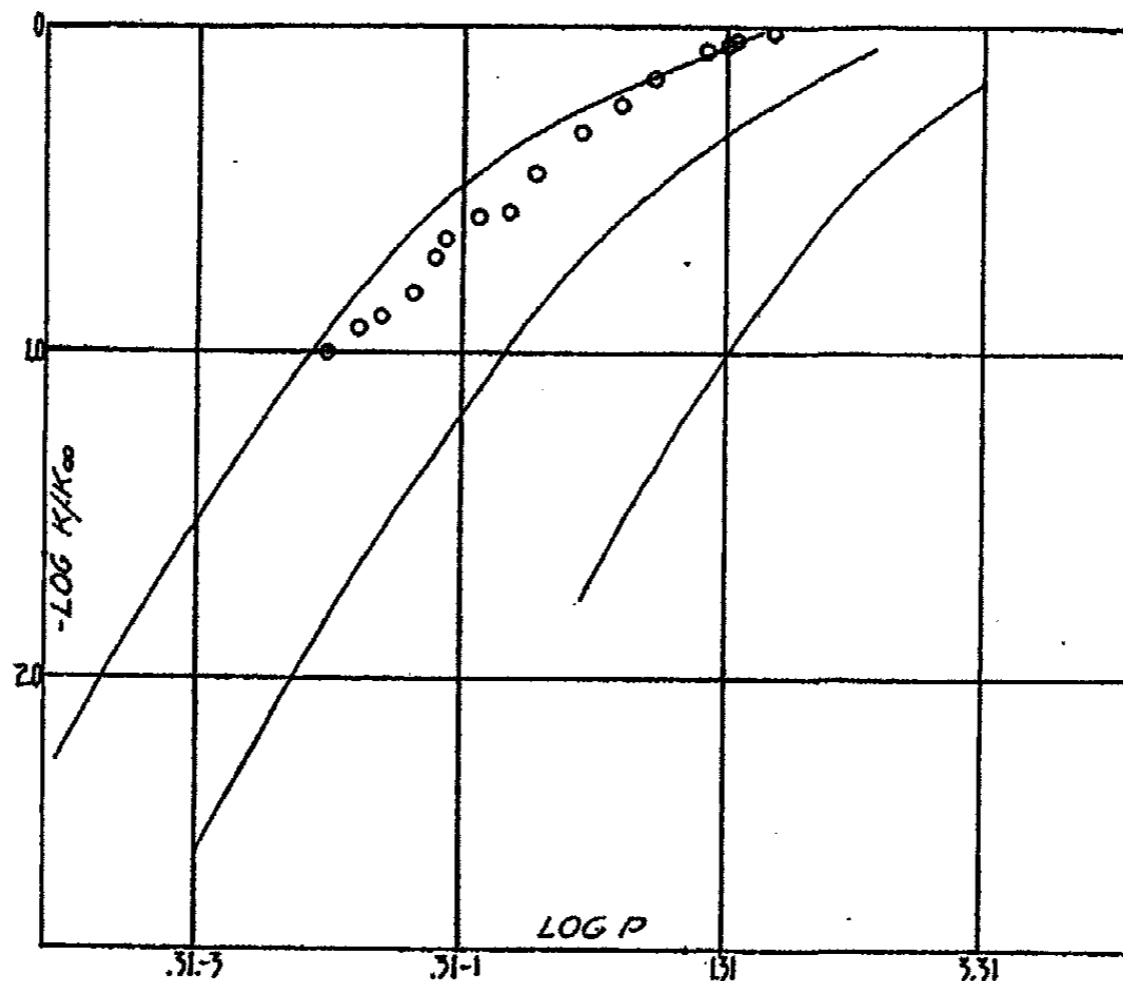


FIG. 2

The lines are the theoretical curves for $s = 12$, $s = 9$, $s = 6$ respectively ($T = 603^\circ$, $\sigma^2 = 1.5 \times 10^{-14}$). A horizontal displacement of these curves corresponds to a change in the value of σ^2 . The points represent some of Ramsperger's experiments on azomethane at 603°K . A vertical displacement of these points corresponds to a change in the assumed value of K_∞ .

may be excited; thus the specific heat data would not be of value in fixing a value for s , since they apply to molecules with much lower internal energy. As for the value given for σ^2 , it must not be forgotten that this is the molecular diameter for collisional deactivation, which need not be the same as the diameter as determined by measurements of viscosity or thermal conductivity; indeed, the experiments of Stuart¹⁸ with mercury vapor have shown that in that case at least the diameter for collisional deactivation is about three times the normal kinetic theory diameter.

Three other unimolecular reactions are known in which the specific reaction rate decreases with decreasing pressure, the decompositions of propaldehyde, of diethyl ether, and of dimethyl ether. In Fig. 4 are given the

¹⁸ Z. Physik, 32, 262 (1925).

plots of $\log K$ against $\log P$ for these reactions. For propaldehyde the curve is similar in form to the theoretical curves, but in order to reconcile the others with the theory it is necessary to assume that in the case of dimethyl ether the highest pressures used have been somewhat insufficient to give K while for diethyl ether the insufficiency must have been still greater. In order to decide this point, the reaction rate would need to be measured for these sub-

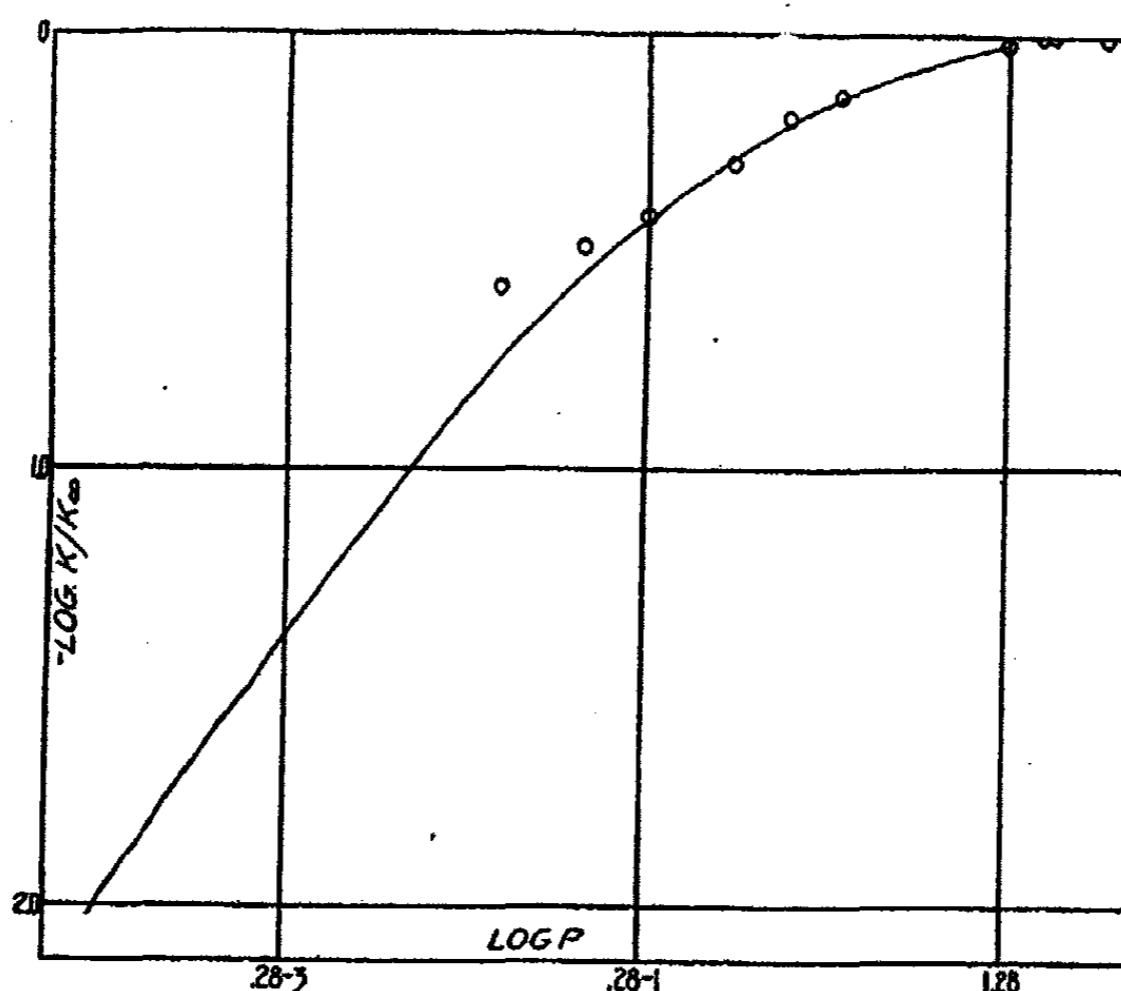


FIG. 3

The curve is drawn for $s = .12$, $\sigma^2 = 1.5 \times 10^{-14}$, $T = 563^\circ$. The points are some of the experimental results on azomethane at 563°K .

stances at pressures up to about five atmospheres. Unless it should be proved that the reaction rate does not increase further with increasing pressure, none of these results can be considered to be in disagreement with the theory.

The only other unimolecular reaction which has been studied at low pressures is the decomposition of nitrogen pentoxide. It seems wise to refrain from theories of this reaction until it has been further studied experimentally. If the rate actually does increase at very low pressures, in the way found by Hirst and Rideal¹⁹ it is probably because some other mechanism of reaction is becoming the dominating factor. Until more is known about this phase of the reaction it is useless to guess what this low-pressure reaction is like. Even the maintenance of the rate down to pressures of about .1 cm is hard

¹⁹ Proc. Roy. Soc., 109A, 526 (1925).

to account for. A rough calculation was made, taking $S = 7$, $\sigma^2 = 10^{-14}$ and $T = 300$. The results were

| | | | | |
|----------------|------|------|------|-------|
| P | 1500 | 15 | .15 | .0015 |
| K/K_{∞} | .994 | .891 | .249 | .0178 |

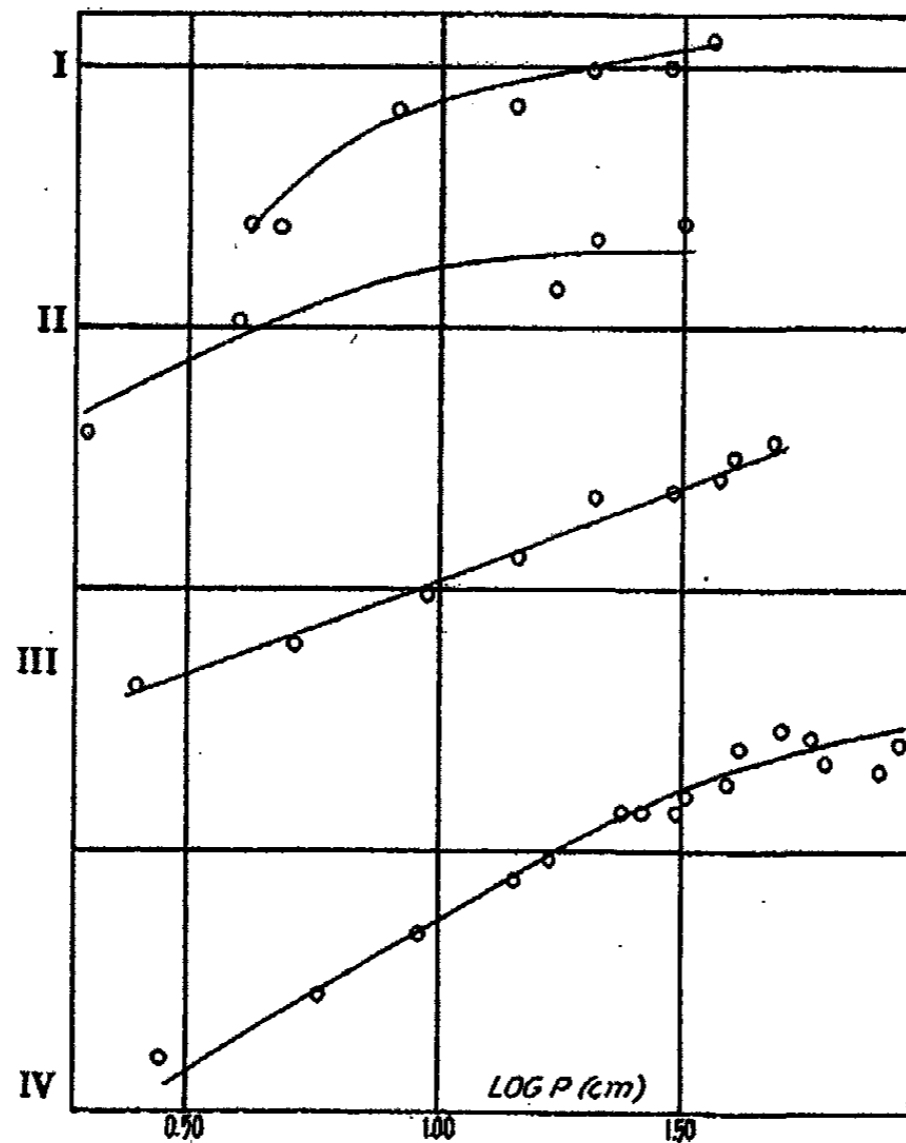


FIG. 4

The points give some of the experimental data for propaldehyde at 849° (I) and at 796° (II), for diethyl ether at 798° (III), and for dimethyl ether at 777° (IV). The ordinates are $\log K$, the distance between the horizontal lines being .5 unit, but the relative vertical positions of the curves are not significant.

Thus at a pressure of .15 cm the reaction rate has fallen to a fourth of its high pressure value. Hence it would be necessary either to take s greater than 7, or to assume a molecular diameter of more than 10^{-7} to account for the experimental results.

Discussion

The results which have been presented here seem to show that the simple type of theory which assumes a single specific reaction rate for all molecules is not satisfactory; this is the theory that Rice and Ramsperger have called

Theory I. Of the four reactions now known in which the specific reaction rate decreases with decreasing pressure, only the decomposition of propaldehyde was known to show this decrease at the time Rice and Ramsperger submitted their paper, and the experiments on this substance have not been extensive enough to reveal the inadequacy of the simple theory. But when it is attempted to apply this theory to the decompositions of diethyl and dimethyl ethers, and of azomethane, it is found unsatisfactory; this is shown by the curves of Fig. 1, which should be straight lines if Theory I is correct. There is every reason to believe that, if the experiments on propaldehyde were extended to lower pressures, here too the r/K , $1/P$ plot would curve.

It thus appears necessary to resort to a theory in which the specific reaction rate increases with the energy; there are now two such theories available, the one developed by Rice and Ramsperger, and called by them Theory II, and the one presented here, which may be called Theory III. These two are very similar: in the development of Theory II it is assumed that decomposition takes place whenever some single degree of freedom in the molecule acquires energy in excess of a critical amount; in Theory III, it is assumed that it is some particular bond (two degrees of freedom) rather than some single degree of freedom which must acquire the critical energy. In the development of the theories certain simplifying assumptions have been made. The discussion of these assumptions which Rice and Ramsperger have given is so good that it seems useless to consider them further here; the same assumptions occur in both theories.

It seems to the author that the physical basis for Theory III is perhaps a little better than for Theory II; rupture of the molecule might be expected to follow at a bond of the critical energy, and a bond represents *two* degrees of freedom. But such arguments are not conclusive and a decision between the two must rest upon experimental evidence. It is to be hoped that in the near future Rice and Ramsperger will attempt to apply their theory to azomethane. It is possible that the two theories will prove sufficiently different to decide between them by a careful application to this reaction.

As to the details of the theories, there is a considerable chance for change. It may be possible to avoid some of the assumptions that have been made, particularly in the calculation of b_E , but this would not be expected to produce any considerable change; the rotational energy might be more explicitly considered, though this would probably be very difficult, or a quantum treatment might be given. None of these changes could modify the general character of the theory.

Summary

1. Reasons have been adduced in support of the definition of energy of activation, due to G. N. Lewis, as the minimum internal energy which molecules must have in order to react.

2. It has been shown that the theory treated by Hinshelwood, and further developed by Rice and Ramsperger, which these authors have called Theory I, in which it is assumed that all activated molecules have the same specific reaction rate, regardless of their energy content, is in disagreement with the experimental results for the decompositions of diethyl ether, dimethyl ether and azomethane.

3. On the basis of statistical mechanics an expression has been deduced for the variation of the specific reaction rate of activated molecules with their energy content.

4. By the use of this expression, an equation has been derived which gives the specific reaction rate for a unimolecular reaction at any pressure.

5. This equation has been shown to be in quantitative agreement with the experimental results for the decomposition of azomethane.

6. The differences between this theory and the similar one just published by Rice and Ramsperger (Theory II) have been pointed out.

Note added in proof: Attention is specially called to the fact that the term degree of freedom is used in this paper in the same sense as it has been used by Rice and Ramsperger. This disagrees with the customary usage, according to which an oscillator has only a single degree of freedom, although it possesses both kinetic and potential energy. As the term is used here, an oscillator has two degrees of freedom.

It is evidently necessary to discuss in more detail the theory of Fowler and Rideal (ref. 12). It was pointed out by Tolman, Yost and Dickinson (ref. 13) that this theory required very large diameters for collisional deactivation to account for the reaction rate of nitrogen pentoxide. It has since been shown by Bernard Lewis²⁰ that there is a numerical error in these calculations, and that the necessary diameters are not as large as Tolman, Yost and Dickinson had supposed. They are, however, very large; to make the rate of production of activated molecules equal to the rate of reaction at 300° K. and a pressure of .05 mm., it is necessary to assume a diameter of 6×10^{-6} cm, which is certainly very large. A still larger diameter would be necessary to maintain the reaction rate at its full value at this pressure, and this is necessary, since the recent work of Hibben²¹ shows that the rate is surely maintained at a pressure of .03 mm. and probably at one ten-fold lower. Lewis's suggestion that this large diameter is "apparent and not real" and that if we take into account the fact that every collision involving an activated molecule does not result in its destruction we will find smaller deactivational diameters, seems to the author to be entirely incorrect. We can calculate the necessary rate of production of activated molecules from the rate of reaction. If we set this equal to a rate of collisional deactivation, we get a number of collisions from which

²⁰ Science, 66, 331 (1927).

²¹ Proc. Nat. Acad. Sci., 13, 626 (1927).

we calculate a diameter; but if only some of the collisions are effective, since the number of effective ones is prescribed for us, we must have more collisions altogether, and hence larger diameters. The idea of a target area is one to which the author subscribes, but it cannot lead to decreased diameters.

Lewis has made calculations for azomethane²² similar to those for nitrogen pentoxide and has, remarkably enough, succeeded in accounting for a rate of activation so large as to permit of the maintenance of specific rate in this reaction at pressures much lower than those at which Ramsperger subsequently found the rate was not maintained.

*The University of Chicago,
July 23, 1927.*

²² Proc. Nat. Acad., 13, 546 (1927).

THE CATALYTIC DECOMPOSITION OF SODIUM HYPOCHLORITE SOLUTIONS*

I. Mechanism of the Reaction

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BY JOHN R. LEWIS

Until recently no systematic study of the catalytic decomposition of sodium hypochlorite solutions had been carried out. In 1923 and 1926, however, articles by Howell¹ and Chirnoaga² were published in which appeared their results using cobalt peroxide as catalyst. Howell assumed that the decomposition rate follows the unimolecular law; but pointed out that the constant (K) increases as the reaction proceeds. He showed that the rate increases in the presence of sodium ions while hydroxyl ions have the opposite effect. Chirnoaga, on the other hand, obtained more concordant results by using the equation $-dc/dt = Kc^{1/n}$ (where c is the concentration, t the time in minutes, K and n constants). This is especially true in those cases where the catalyst was very active. In other cases, i. e. where the catalyst was less active the unimolecular law held. In general the work of the above mentioned investigators has been confirmed in this laboratory but it appeared that the mechanism of the decomposition can be explained more simply by using the equation $dc/dt = K$; for when the volume of the evolved oxygen, in cubic centimeters, was plotted against the time, in minutes, a straight line was obtained. This linear relationship held in most cases from ten to twenty percent of the total reaction.

These results suggested a mechanism similar to that found by Armstrong³ and by Armstrong and Hilditch⁴ for the hydrolysis of sugar solutions by enzymes and for the hydrogenation of certain unsaturated organic esters using nickel as catalyst. In the paper⁵ on the action of enzymes on sugar it was shown that equal quantities of sugar were hydrolyzed in equal time intervals. A similar relationship was obtained in the hydrogenation experiments. While the linear portion of the curve covered approximately ten percent of the total reaction in the case of the sugar hydrolysis, the linear portion of the curve in the hydrogenations held fairly well from fifty to eighty percent of the total reaction. Among other examples of reactions of this type may be mentioned the results of Bredig and von Berneck⁶ who found that $dc/dt = K$ for the decomposition of hydrogen peroxide by colloidal platinum, and also the experiments of Hinshelwood⁷ on the decomposition of certain gases at the sur-

*Contribution from the Laboratories of General Chemistry of the University of Wisconsin.

¹ Howell: Proc. Roy. Soc., 104A, 134 (1923).

² Chirnoaga: J. Chem. Soc., 1926, 1683.

³ Armstrong: Proc. Roy. Soc., 73, 500 (1904).

⁴ Armstrong and Hilditch: Proc. Roy. Soc., 98A, 27 (1920).

⁵ Armstrong: Proc. Roy. Soc., 73, 500 (1904).

⁶ Bredig and von Berneck: Z. physik. Chem., 31, 266 (1899).

⁷ Hinshelwood: "Kinetics of Chemical Change in Gaseous Systems," 148 (1926).

faces of hot wires. Reactions of this type are usually spoken of as zero order reactions.

The conditions necessary for the realization of zero order reactions may be stated as follows:

1. Comparatively high concentration of the substance undergoing change.
2. The catalyst should maintain its activity.
3. There should be small quantities of catalyst in order that the active mass, i. e. the adsorbed reactant on the catalyst is small compared with the bulk of reactant.
4. The decomposition of the reactant-catalyst complex must be the slow reaction, thus insuring at all times a catalyst surface completely covered with reactant.

Experimental

Preparation of Materials:

1. Sodium hypochlorite solutions were prepared as follows: Approximately normal sodium hydroxide, prepared by the action of metallic sodium on distilled water, was treated with pure chlorine. The gas was allowed to bubble slowly through the sodium hydroxide solution, the container of which was kept cool by immersion in an ice bath. The progress of the reaction was determined from time to time by pipeting out two cubic centimeters of the solution, destroying the sodium hypochlorite by means of neutralized hydrogen peroxide, and titrating the excess alkali with standard acid. The reaction was stopped when the hypochlorite solution contained but a slight excess of free sodium hydroxide. The sodium hypochlorite was determined by adding a known quantity of the solution to an acidified potassium iodide solution, and titrating the freed iodine with standardized sodium thiosulfate. The initial concentrations of the hypochlorite solutions prepared are as follows:

| Solution | Concentration of NaClO | Concentration of NaOH |
|----------|---------------------------|--------------------------|
| 1 | 29.74 gr. per L | 0.13 Normal |
| 2 | 37.76 gr. " " | 0.03 " |
| 3 | 56.48 gr. " " | 0.11 " |
| 4 | 46.55 gr. " " | 0.032 " |

2. The catalysts solutions were made from recrystallized salts; standard stock solutions of copper sulfate, ferric sulfate and cobalt sulfate being made. The cobalt peroxide, copper oxide, and iron oxide suspensions were made according to the method of Howell¹ and Chirnoaga² except that the precipitated oxides were washed by decantation in every case rather than by filtering. This process was continued until the wash water was practically free from alkali, requiring in some cases three or four weeks.

¹ Howell: Proc. Roy. Soc., 104A, 134 (1923).

² Chirnoaga: J. Chem. Soc., 1926, 1693.

Apparatus and Method of Experimentation

The apparatus used for the first experiments was essentially the same as that devised and used by Walton¹ and his students for their studies in chemical kinetics. Twenty-five cubic centimeters of the sodium hypochlorite and the catalysts (usually 1 c.c.) were placed in especially designed reaction flasks supported by a shaking device in a thermostat. The catalyst was either placed in a glass capsul held in the neck of the flask until the desired moment, when it was allowed to fall into the hypochlorite solution; or pipeted directly into the reaction flask through a short side-neck which was immediately closed. At the instant the catalyst was mixed with the hypochlorite, a stop-watch and the shaker were started. Readings of the evolved oxygen, collected in water-jacketed burets, were taken at suitable intervals of time until the reaction was complete.

Calculations

The data for tabulation in the tables which follow were obtained by the following equations. Equation (1) is the so-called zero-order equation, equation (2) the ordinary unimolecular expression, and (3) which is one form of the well known Freundlich Adsorption equation used by Chirnoaga¹ in his hypochlorite studies.

$$(1) \quad K = dx/dt \text{ or more simply } K = x/t$$

where x is the c.c. of oxygen evolved in time (t) expressed in minutes.

$$(2) \quad K_1 = \frac{2.303}{t} \log \frac{C_0}{C_0 - C_t}$$

where t is the time in minutes, C_0 is the concentration of hypochlorite expressed in cubic centimeters of oxygen at zero time, and C_t is the concentration after time t .

$$(3) \quad K_2 = \frac{1}{t} \frac{(C_0^{N-1/N} - C_t^{N-1/N})N}{N-1}$$

where C_0 and C_t and t are the same as in (2) and N is a constant.

Preliminary Results

The effect of the rate of shaking of the reaction mixture on the rate of oxygen evolution was determined. The following table gives the results.

TABLE I

| Experiment Number | Number of shakes per minute | c.c. of oxygen after 20 minutes | K |
|-------------------|-----------------------------|---------------------------------|-------|
| 1 | 400 | 4.3 | 0.215 |
| 2 | 630 | 6.6 | 0.33 |
| 3 | 800 | 8.15 | 0.407 |
| 4 | 1190 | 8.1 | 0.405 |

¹ Walton: *Z. physik. Chem.*, 47, 185 (1904).

It will be observed that the values for the last two agree well, showing that rates of 800 or above give concordant results. All subsequent experiments were carried out with the rate of shaking at 800 or more per minute.

It was found that glass or Bakelite beads placed in the reaction flasks to prevent supersaturation, retarded the reaction rate. This was caused in the

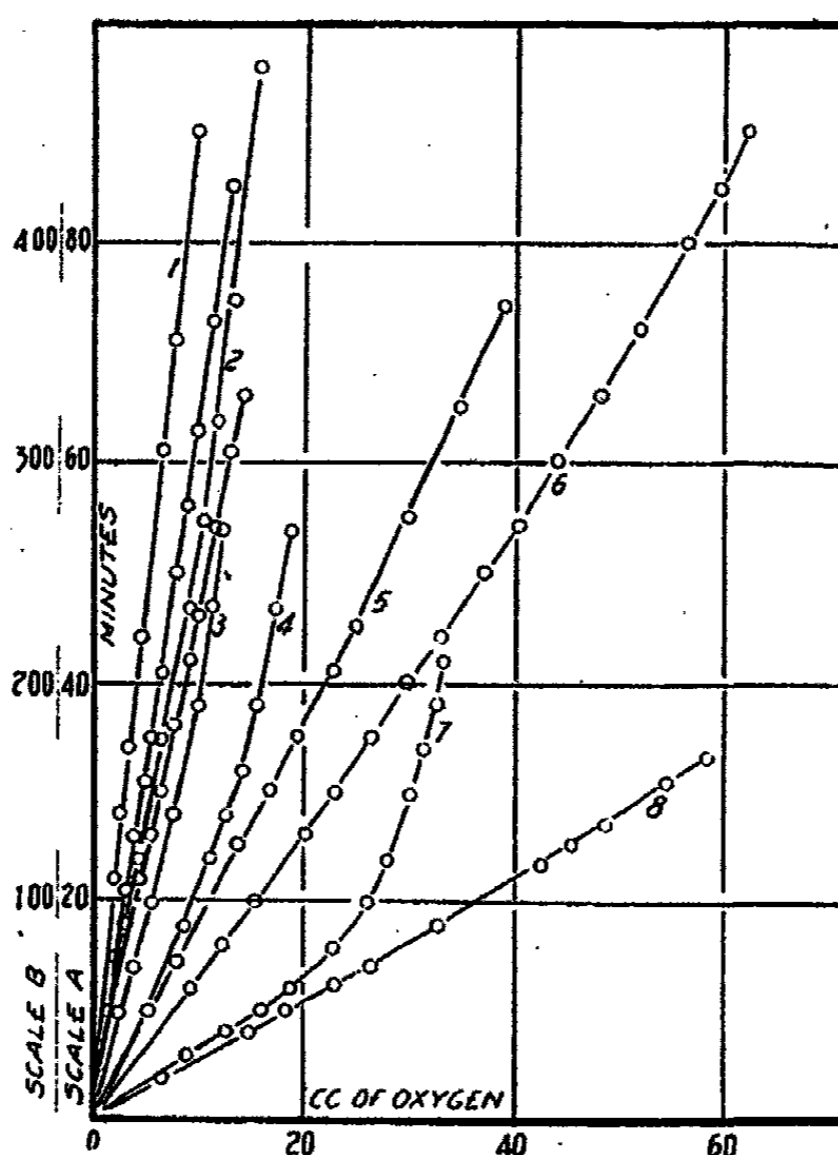


FIG. 1

Decomposition of sodium hypochlorite solutions using various catalysts.

- Scale A = 1. Copper oxide
 2. Copper sulfate
 3 and 4. Mixtures of copper and ferric oxides
 5. Cobalt sulfate
 6. Cobalt peroxide at 45°C.
 Scale B = 7. Mixed copper and ferric oxides
 8. Cobalt peroxide at 35°C.

case of the Bakelite by a chemical reaction between the hypochlorite and the Bakelite. The glass beads cut down the rate of hypochlorite decomposition by holding the catalyst particles mechanically on the bead surfaces.

Results

The results obtained using the above equations as a basis for calculating the rate of decomposition are given in the following tables. In order to conserve space, duplicate results (obtained in all cases) are not given.

Tables II and III are for cobalt peroxide at 45°C and 35°C, while Table IV is for cobalt sulfate solution. Tables V and VI give the results obtained for

copper sulfate solution and for precipitated copper oxide. Finally in Tables VII, VIII and IX are given the results for mixed oxides of iron and copper. In Tables IV, V, VII, VIII and IX the catalysts were added in the solution form. Due to the alkalinity of the hypochlorite solutions, the catalyst solutions reacted, forming the desired oxides. Data for the decomposition of the hypochlorite using precipitated iron oxide only are not given since the decomposition rate is so slow that it may be considered as without effect. In the tables (t), (x), (K), (K₁), and (K₂) have the same significance as in the equations. The data given in the tables are also presented graphically in Fig. 1.

TABLE II

Temp. 45°C. C₀ = 160 Catalyst: 1 c.c. cobalt peroxide 1/n = 0.8
peroxide (0.215 gr. per L)

| t | x | K | K ₁ | K ₂ |
|-----|-------|------|----------------|----------------|
| 10 | 7.05 | .705 | .00462 | .0125 |
| 14 | 10.06 | .755 | .00461 | .0128 |
| 18 | 13.2 | .734 | .00486 | .0133 |
| 24 | 18.5 | .770 | .00512 | .0139 |
| 37 | 27.6 | .745 | .00513 | .0140 |
| 44 | 32.8 | .745 | .00521 | .0140 |
| 50 | 37.1 | .743 | .00531 | .0142 |
| 55 | 41.2 | .747 | .00543 | .0145 |
| 66 | 48.0 | .728 | .00543 | .0149 |
| 72 | 52.0 | .723 | .00546 | .0145 |
| 85 | 59.8 | .705 | .00552 | .0146 |
| 90 | 62.6 | .696 | .00553 | .0145 |
| 95 | 66.3 | .697 | .00563 | .0148 |
| 100 | 69.0 | .696 | .00565 | .0147 |
| 104 | 70.8 | .681 | .00564 | .0146 |

TABLE III

Temp. 35°C. C₀ = 160. Catalyst: 1 c.c. cobalt peroxide 1/n = 0.8

| t | x | K | K ₁ | K ₂ |
|-----|-------|------|----------------|----------------|
| 10 | 2.95 | .295 | .00182 | .0055 |
| 20 | 6.46 | .322 | .00207 | .00587 |
| 30 | 10.56 | .351 | .00225 | .00616 |
| 40 | 14.5 | .362 | .00240 | .00624 |
| 50 | 18.2 | .364 | .00244 | .00620 |
| 62 | 22.8 | .368 | .00252 | .00685 |
| 71 | 26.03 | .367 | .00250 | .00663 |
| 82 | 30.2 | .368 | .00258 | .00654 |
| 95 | 34.6 | .354 | .00257 | .00678 |
| 108 | 39.4 | .365 | .00260 | .00686 |
| 117 | 42.5 | .363 | .00263 | .00697 |
| 136 | 48.6 | .357 | .00266 | .00692 |
| 142 | 50.1 | .353 | .00266 | .00712 |
| 155 | 54.9 | .354 | .00270 | .00709 |

TABLE IV

Temp. 35°C. $C_0 = 112$. 1 c.c. CoSO_4 solution $1/n = 0.8$
containing 1.72 gr. per L.

| t | x | K | K_1 | K_2 |
|----|-------|------|--------|-------|
| 14 | 7.13 | .509 | .00476 | .0110 |
| 20 | 10.7 | .535 | .00494 | .0127 |
| 28 | 15.35 | .548 | .00517 | .0135 |
| 33 | 18.1 | .548 | .00534 | .0136 |
| 41 | 22.5 | .549 | .00545 | .0138 |
| 51 | 27.7 | .543 | .00557 | .0139 |
| 55 | 29.8 | .542 | .00561 | .0140 |
| 61 | 32.61 | .535 | .00568 | .0141 |
| 65 | 34.6 | .533 | .00568 | .0141 |
| 70 | 37.0 | .528 | .00572 | .0146 |

TABLE V

Temp. 35°C. $C_0 = 35.8$. 1 c.c. CuSO_4 containing $1/n = 0.8$
0.6 gr. Cu. per L.

| t | x | K | K_1 | K_2 |
|-----|------|------|--------|-------|
| 14 | 2.2 | .157 | .00452 | .0089 |
| 20 | 3.42 | .171 | .00512 | .0100 |
| 30 | 5.46 | .182 | .00556 | .0109 |
| 40 | 7.5 | .187 | .00588 | .0116 |
| 55 | 10.1 | .183 | .00603 | .0119 |
| 64 | 11.5 | .180 | .00605 | .0118 |
| 75 | 13.1 | .174 | .00607 | .0118 |
| 91 | 15.3 | .160 | .00609 | .0116 |
| 125 | 18.9 | .151 | .00601 | .0114 |
| 148 | 20.7 | .140 | .00584 | .0110 |
| 194 | 24.1 | .124 | .00575 | .0105 |

TABLE VI

Temp. 35°C. $C_0 = 35$. 5 c.c. copper oxide containing $1/n = 0.8$
0.832 gr. Cu per L.

| t | x | K | K_1 | K_2 |
|-----|-------|------|--------|--------|
| 15 | 2.28 | .152 | .00444 | .00900 |
| 26 | 4.07 | .156 | .00477 | .00960 |
| 35 | 5.61 | .160 | .00500 | .0100 |
| 50 | 7.9 | .158 | .00514 | .0102 |
| 56 | 8.9 | .159 | .00526 | .0103 |
| 73 | 11.3 | .155 | .00534 | .0104 |
| 85 | 12.8 | .156 | .00536 | .0104 |
| 99 | 14.7 | .149 | .00550 | .0105 |
| 107 | 15.55 | .146 | .00548 | .0105 |
| 260 | 26.85 | .104 | .00559 | .00978 |

TABLE VII

Temp. 35°C. $C_0 = 35.8$. 1 c.c. of catalyst $\left\{ \begin{array}{l} 0.6 \text{ gr. Cu per L. } \\ 0.064 \text{ gr Fe per L. } \end{array} \right. \quad 1/n = 0.8$

| t | x | K | K_1 | K_2 |
|----|------|------|--------|--------|
| 10 | 2.71 | .271 | .00785 | .00585 |
| 14 | 3.94 | .281 | .00824 | .0170 |
| 18 | 5.00 | .278 | .00842 | .0168 |
| 20 | 5.5 | .275 | .00830 | .0167 |
| 22 | 6.06 | .275 | .00842 | .0168 |
| 24 | 6.53 | .272 | .00834 | .0167 |
| 28 | 7.46 | .267 | .00838 | .0166 |
| 38 | 9.76 | .257 | .00836 | .0166 |
| 47 | 11.0 | .234 | .00783 | .0153 |
| 54 | 12.2 | .226 | .00722 | |

TABLE VIII

Temp. 35°C. $C_0 = 35$. 1 c.c. of catalyst $\left\{ \begin{array}{l} .6 \text{ gr. Cu per L. } \\ .128 \text{ g Fe " " } \end{array} \right. \quad 1/n = 0.8$

| t | x | K | K_1 | K_2 |
|----|------|------|--------|-------|
| 6 | 2.95 | .492 | .01485 | .0300 |
| 10 | 5.4 | .54 | .01660 | .034 |
| 14 | 7.22 | .516 | .01655 | .0332 |
| 18 | 8.95 | .496 | .01635 | .0328 |
| 20 | 9.67 | .483 | .01616 | .0320 |
| 24 | 11.0 | .458 | .01572 | .0311 |
| 28 | 12.2 | .437 | .01530 | .030 |
| 32 | 13.8 | .433 | .01568 | .0278 |
| 38 | 15.2 | .40 | .01502 | .0289 |
| 47 | 17.0 | .362 | .01415 | .0275 |
| 54 | 18.5 | .342 | .01393 | .0264 |

TABLE IX

Temp. 35°C. $C_0 = 35.8$. 1 c.c. of catalyst $\left\{ \begin{array}{l} .6 \text{ gr Cu } \\ .192 \text{ gr Fe } \end{array} \right. \quad \begin{array}{l} \text{per L.} \\ \text{" " } \end{array} \quad 1/n = 0.8$

| t | x | K | K_1 | K_2 |
|----|-------|-------|-------|-------|
| 6 | 8.7 | 1.45 | .0464 | .0916 |
| 8 | 12.6 | 1.57 | .0542 | .1062 |
| 10 | 15.6 | 1.56 | .0572 | .1105 |
| 12 | 18.2 | 1.52 | .0591 | .1120 |
| 18 | 24.2 | 1.34 | .0624 | .1140 |
| 20 | 25.8 | 1.29 | .0637 | .1150 |
| 24 | 27.7 | 1.15 | .0620 | .1100 |
| 30 | 29.64 | 0.99 | .0587 | .1020 |
| 34 | 31.15 | 0.916 | .0602 | .101 |
| 38 | 32.3 | 0.850 | .0606 | .099 |
| 42 | 32.9 | 0.784 | .0503 | .0963 |

Discussion

Upon examination of the above tables it will be noted that the values for $K = x/t$ remain fairly constant for a time but fall off after twenty or thirty percent of the reaction is completed. On the other hand values for K_1 , the unimolecular constant, increase as the reaction proceeds. This is true in all

cases. However in Tables VII, VIII and IX giving the data for mixed oxides of iron and copper it will be noted that K_1 falls after an initial increase. Upon examination of the values obtained by using equation (3) it will be apparent that the results are more concordant than those obtained using the unimolecular equation; but they also increase or decrease, paralleling the K_1 values.

It will be observed in Tables VII, VIII and IX that the mixed oxides show a marked "promoter effect" on the decomposition rate. K and K_1 values given in Table VII are good but those in Tables VIII and IX are somewhat irregular. It is proposed to extend this phase of the investigation.

The Decomposition of Sodium Hypochlorite Solutions when a Constant Fresh Supply of Hypochlorite was allowed to pass over a Fixed Amount of Catalyst.

In order to obtain more information concerning the mechanisms of the decomposition of sodium hypochlorite solutions, the following additional experiments were performed.

The apparatus shown in Fig. 2 was used for this work. The hypochlorite from a storage bottle was allowed to enter drop by drop into the inner vessel D through the tube B. The volume of the liquid in D being kept constant by holding its level at C. The hypochlorite passed through the sintered glass filter E and was collected in F. The pores of this filter¹ however were suffi-

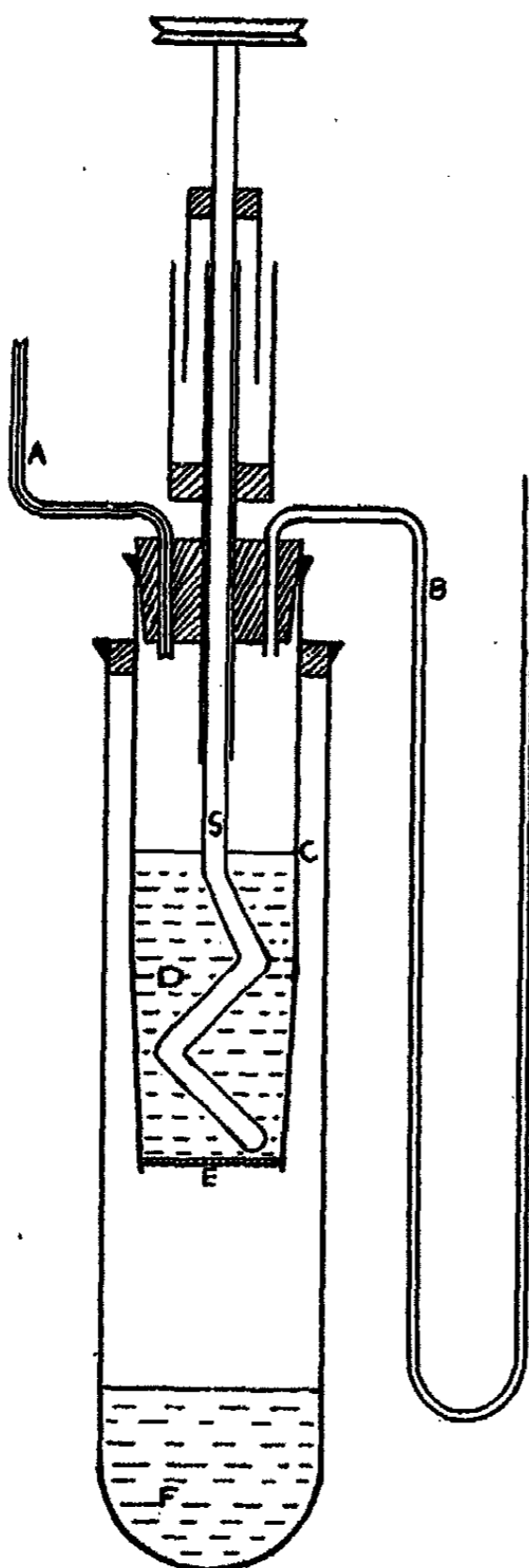


FIG. 2
Apparatus used in measuring the decomposition of NaClO solutions.

¹ This apparatus was made from a Jena glass crucible obtained from the Empire Laboratory Supply Co., 218-220 E. 37th St., New York.

ciently small to prevent the passage of catalyst particles. The oxygen liberated passed through the tube A and was collected and measured in water-jacketed burets. The stirrer S operating at 550 revolutions per minute, worked through an ordinary mercury seal. The apparatus was immersed in a water bath at constant temperature.

In passing through this apparatus the hypochlorite solution changed in concentration from ten to twenty percent. The following tables give the results obtained. Cobalt peroxide, the only catalyst used in these experiments was of the same concentration as that used in Table II. Solutions used to obtain the data in Tables X, XI and XII were made by diluting the original stock solution with distilled water. The values given are for cubic centimeters of oxygen at 0°C and 760 mm. pressure; *t*, *x* and K having the notations used in the previous tables. *C*₁ refers to the initial concentration of the hypochlorite in grams per liter. Fig. 3 expresses the same results graphically.

TABLE X

Temp. 30°C. *C*₁ = 46.5 gr. NaClO per L. 1 c.c. cobalt peroxide

| <i>t</i> | <i>x</i> | K | <i>t</i> | <i>x</i> | K |
|----------|----------|------|-----------|----------|------|
| | | | Duplicate | | |
| 5 | 1.33 | .265 | 5 | 1.43 | .285 |
| 11 | 3.02 | .274 | 10 | 2.85 | .285 |
| 15 | 4.12 | .274 | 15 | 4.03 | .268 |
| 20 | 5.54 | .276 | 20 | 5.54 | .276 |
| 25 | 6.8 | .272 | 25 | 6.6 | .264 |
| 30 | 7.95 | .266 | 30 | 8.1 | .271 |
| 35 | 9.28 | .266 | | | |
| 40 | 10.7 | .268 | | | |
| 45 | 12.1 | .268 | | | |

*C*₁ = 39.6 gr. NaClO per L.

| | | |
|----|------|------|
| 5 | 1.38 | .277 |
| 10 | 2.78 | .278 |
| 15 | 4.05 | .269 |
| 20 | 5.47 | .273 |
| 25 | 6.9 | .276 |
| 30 | 8.05 | .268 |

*C*₁ = 34.2 gr. NaClO per L.

| | | |
|----|------|------|
| 5 | 1.43 | .287 |
| 10 | 2.8 | .280 |
| 15 | 4.05 | .270 |
| 20 | 5.37 | .269 |
| 25 | 6.65 | .266 |
| 35 | 7.94 | .265 |
| 35 | 9.28 | .265 |

*C*₁ = 28 gr. NaClO per L.

| | | |
|----|------|------|
| 5 | 1.34 | .268 |
| 10 | 2.61 | .261 |
| 15 | 3.74 | .249 |
| 20 | 4.80 | .240 |
| 25 | 6.05 | .242 |
| 30 | 7.18 | .239 |

TABLE XI

| Temp. 30° C. $C_1 = 46.5$ gr. NaClO per L. | | | 2 c.c. cobalt peroxide | | |
|--------------------------------------------|-------|------|------------------------|-----------|------|
| t | x | K | t | x | K |
| | | | | Duplicate | |
| 5.0 | 2.82 | .563 | 5 | 2.78 | .556 |
| 10 | 5.57 | .557 | 10 | 5.5 | .550 |
| 15 | 8.25 | .550 | 15 | 8.3 | .553 |
| 20 | 10.94 | .548 | 20 | 11.0 | .550 |
| 25 | 13.5 | .543 | 25 | 13.6 | .544 |
| 30 | 16.2 | .540 | 30 | 16.3 | .543 |

TABLE XII

| Temp. 40° C. $C_1 = 46.5$ gr. NaClO per L. | | | 1 c.c. cobalt peroxide | | |
|--------------------------------------------|-------|------|------------------------|-----------|------|
| t | x | K | t | x | K |
| | | | | Duplicate | |
| 5 | 2.68 | .536 | 5 | 2.68 | .536 |
| 10 | 5.44 | .544 | 10 | 5.4 | .540 |
| 15 | 8.21 | .548 | 15 | 8.16 | .544 |
| 20 | 10.9 | .546 | 20 | 10.83 | .543 |
| 25 | 13.61 | .544 | 25 | 13.54 | .543 |
| 30 | 16.26 | .543 | 30 | 16.27 | .542 |

$C_1 = 39.6$ gr. NaClO per L.

| | | |
|----|------|------|
| 5 | 2.67 | .534 |
| 10 | 5.26 | .526 |
| 15 | 7.84 | .523 |
| 20 | 10.6 | .529 |
| 25 | 13.4 | .536 |
| 30 | 16.1 | .537 |

Discussion

Examination of the data presented in Tables X, XI and XII and illustrated graphically in Fig. 3, shows that the rate of decomposition as measured by the equation $K = x/t$ is practically constant over a wide range of concentration. Results obtained with concentrations of 46.5, 39.6 and 34.2 grams of sodium hypochlorite per liter being 0.271, 0.273 and 0.270 respectively. When the concentration of the hypochlorite falls below these values K falls off.

By comparing the results in Tables X and XI it will be observed that the rate of reaction is proportional to the concentration of the catalyst, confirming the observations of Howell¹ and Chirnoaga.²

The temperature coefficient, determined over the range 30° C to 45° C is lower than that determined by Howell. However the value $K_{40}/K_{30} = 2.0$ obtained in the above described apparatus agree well with the value $K_{45}/K_{35} = 2.02$ obtained in the shaker apparatus.

¹ Howell: Proc. Roy. Soc., 104A, 134 (1923).

² Chirnoaga: J. Chem. Soc., 1926, 1693.

The normal temperature coefficient obtained for this reaction indicates that catalytic decomposition of sodium hypochlorite is chemical in nature. If it is assumed that the decomposition is due to the formation of a catalyst-hypochlorite complex and its subsequent decomposition, then the mechanism of the reaction can be pictured as hypochlorite ions or molecules combining with the catalyst forming the addition compound which immediately decom-

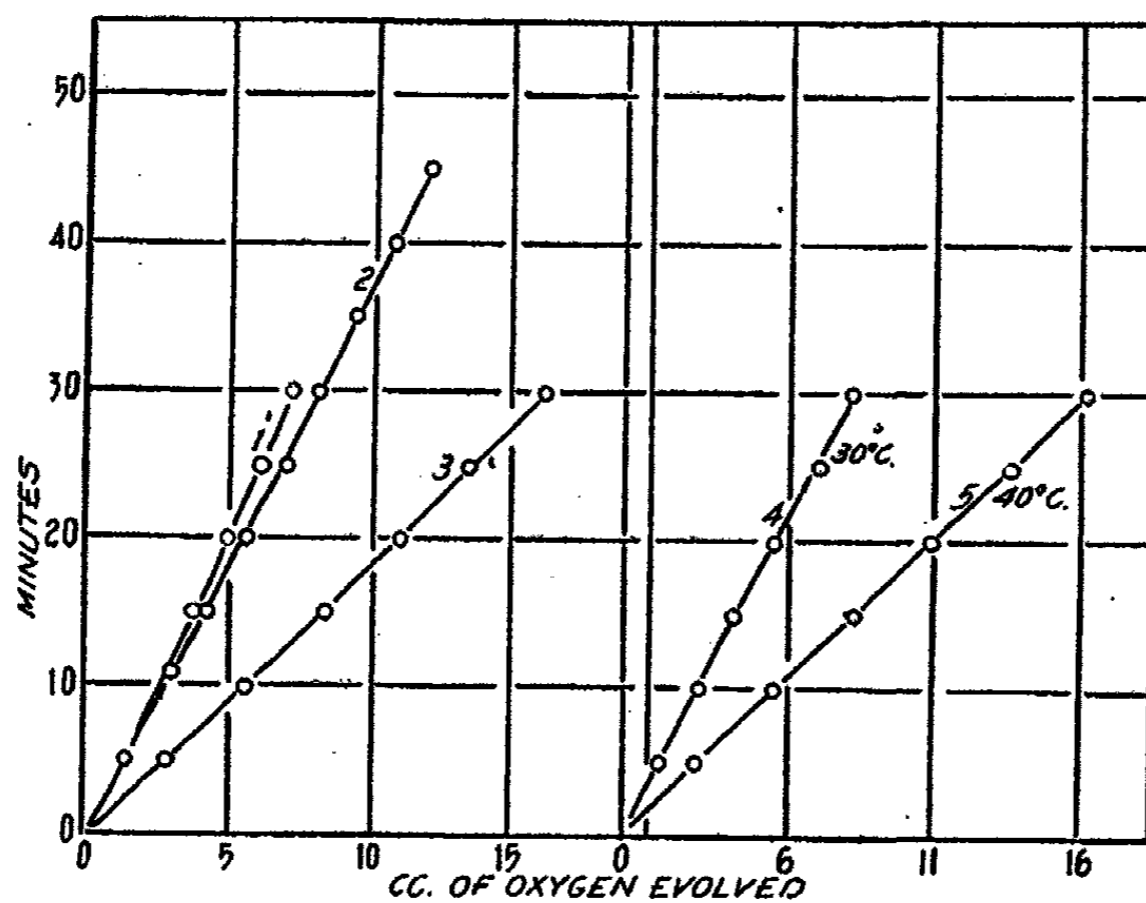


FIG. 3

Decomposition of hypochlorite solutions using apparatus shown in Fig. 2.

(1, 2) and (4) are for solutions containing 28, 46.5, and 39.6 gr, NaClO per liter using 1 cc. cobalt peroxide catalyst at 30°C.

(3) is same as (2) except 2 cc. of catalyst are used. (5) is same as (2) except the temperature was 40°C.

poses. Just as long as the concentration of the hypochlorite is relatively high in comparison with that of the catalyst, the decomposition will take place at a regular rate, for at the moment a catalyst-hypochlorite molecule decomposes another hypochlorite molecule combines with the catalyst, forming another complex which subsequently decomposes. After a time however the rate will fall off due to any one, or combination, of the following causes:

1. Change in the activity of the catalyst caused by changes in its surface.
2. Poisoning of the catalyst; in this case no doubt by hydroxyl ions.
3. A low concentration of the reactant in the solution surrounding the catalyst. Data obtained under such conditions usually fit the unimolecular equation or the Freundlich equation (3 above).

Summary

1. The mechanism of the decomposition of sodium hypochlorite solutions has been studied using cobalt, copper and iron oxides and peroxides as catalysts.

2. The data obtained have been given in tables and shown graphically.
3. It was shown that the decomposition takes place at a regular rate as long as the catalyst is completely covered with reactant.
4. An apparatus has been described suitable for experiments where a constant fresh supply of a reactant solution may be passed over a fixed amount of catalyst.

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MOLECULAR ORIENTATION AT SURFACES OF SOLIDS

I. MEASUREMENT OF CONTACT ANGLE AND THE WORK OF ADHESION OF ORGANIC SUBSTANCES FOR WATER*

BY A. H. NIETZ

The study of solid surfaces has been taken up only recently and has not yet been given the attention it deserves. Some practical applications of the study of wetting power have been made in the flotation process, largely with minerals, of course. A few organic substances have been studied by Adam and Jessop,¹ who have calculated the work of adhesion of several organic solids. In recent years it has come to be realized that molecular orientation at interfaces (polarity of solid surfaces) is intimately connected with the phenomenon of adhesion and with the stability of colloids. The interfacial tension of gelatin and toluene² was shown in this Laboratory to support this view, and in order to obtain more quantitative information on this, Dr. Sheppard suggested to the author an experimental study of the "contact angle" of related organic compounds.

The method used has been known for many years but was never applied to any extent so far as known until the work of Adam and Jessop (loc. cit). Young in 1805³ and Dupré⁴ in 1869 published some of the relations for the contact angle of a liquid against a solid and the work of adhesion between the two.

For the sake of clearness, the development of the method from the equation of Dupré and the work of Young is included here. If we have two bars, each 1 sq. cm., in cross-section, of liquid and solid respectively, represented by L and S in Fig. 1, the work done in separating L from S is

$$W = T_L + T_S - T_{LS}$$

where T_L and T_S are the free energies of the surfaces which have appeared and T_{LS} is the free energy of the interface which has disappeared. Consider next the relations for a drop of liquid L resting in equilibrium on a solid S (Fig. 2). At the point B, we have an equilibrium of forces represented by the equation

$$T_{SA} = T_{SL} + T_{LA} \cos \theta$$

where θ is the angle of contact between the liquid and solid as shown. This

*Communication No. 323 From the Research Laboratory of the Eastman Kodak Company.

¹ J. Chem. Soc., 127, 1863 (1925).

² S. E. Sheppard and S. S. Sweet: J. Am. Chem. Soc., 44, 2797 (1922).

³ "Cohesion of Fluids," (1805).

⁴ "Théorie mécanique de la Chaleur," p. 369 (1869).



$$W = T_L + T_S - T_{LS}$$

WORK OF ADHESION.

FIG. 1

equation can also be derived from purely theoretical considerations. If we now substitute this equation in the Dupré equation, we obtain

$$W = T_{LA} (1 + \cos \theta)$$

which is an expression easily applied to the work of adhesion. It is necessary to make but two measurements, T_{LA} , the surface tension of the liquid in contact with the solid; and θ , the angle of contact of water against the solid. This is the basis of the experimental procedure.

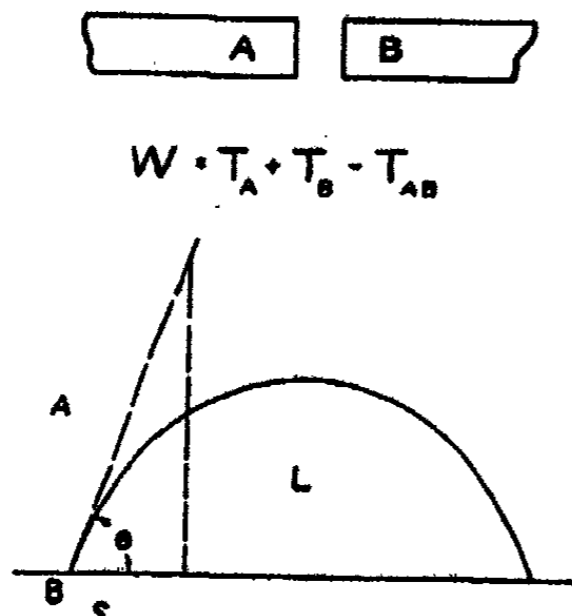


FIG. 2

Experimental Methods

Two practical methods for the measurement of the contact angle have been used. One employs the rotating cylinder described by Ablett,¹ and the other the tilting plate as used by Adam and Jessop and others. The former uses material coated on a silver-plated cylinder, the angle being obtained by adjusting the height of liquid until the liquid-air boundary is straight right up to the line of contact. In the second method a plate was coated with the material and then inclined until the liquid-air interface was perfectly plane, the angle being

measured directly. The second method offers decided advantages and is sufficiently accurate for ordinary work.

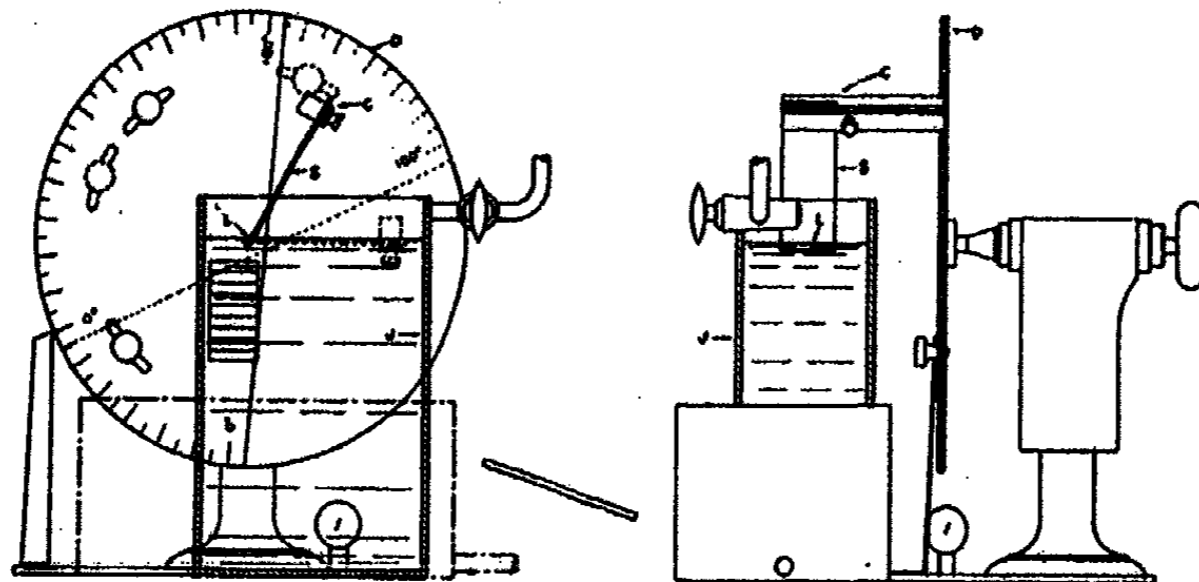
Differences due to unknown causes have been found between the two methods. Though some refinements in Ablett's apparatus have been made and the accuracy increased, his results have not been reproduced in every respect for paraffin, and some mysterious differences occur with other substances when measured by the two method. Time has not permitted a complete investigation which should be made of the causes for these differences.

An attempt was made to check Ablett's results with paraffin. The paraffin used represents a product of very high purity. It was prepared especially for this work by Dr. H. T. Clarke, the treatment consisting of repeated stirring with warm concentrated sulphuric acid, melting at about 100° for several hours in contact with metallic sodium, and final distillation in vacuo. The boiling point of the final product was 218°-225° at 4 mm.

The results with this paraffin gave 109° ± 30' for the angle of contact in water, measured by Ablett's method, and the same by the plate method. This high value in itself would indicate a high degree of purity, i.e., freedom from unsaturated or polar compounds. Ablett's results were verified so far as two sets of values for clockwise and counter-clockwise rotation at various speeds are concerned. But it was not found possible to determine what he calls a "stationary angle," that is, an angle when there is no relative motion of solid with respect to liquid. It would seem next to physically impossible

¹ Phil. Mag., 46, 244 (1923).

to obtain this condition since in an apparatus of Ablett's type it would be necessary to add liquid at *exactly* the same rate as the advance of solid out of the liquid to prevent motion of solid into or out of the liquid. Ablett himself does not specify how these stationary angles could have been obtained. Merely allowing the cylinder to remain motionless and adding water would give a result in the same sense as the solid advancing into the water, or, in the present case, counter-clockwise motion. It is hoped later to make an at-



APPARATUS FOR MEASURING CONTACT ANGLE

FIG. 3

tempt to obtain the necessary condition for a stationary angle, but it is very doubtful that it can easily be secured. Further reference is made below to differences between the cylinder and plate method.

For the present work the plate method was found more rapid and convenient, and the results are believed more reliable, at least until the nature of certain discrepancies is better understood. A special form of apparatus was designed which is very convenient in use and eliminates to some extent the error involved in the motion of the solid in or out of the liquid. This is sketched in Fig. 3. The slide S is an ordinary microscopic slide on which is coated a small quantity of the melted solid. The slide is held by a convenient clamp C so that it can be turned to make various angles with the water as the disk D is turned. The height of the liquid in the jar J is so adjusted and the clamp C is so placed that the line of contact L is on the axis of rotation of the disk D. This disc has a carefully graduated metal scale affixed to its surface in such a way that it can be adjusted. When an adjoining pointer indicates zero degrees, the slide S should be in a horizontal position as shown by a small spirit level placed on it. The disk is mounted to the chuck of a small jeweller's lathe which permits smooth turning and accurate centering.

By the use of this apparatus, therefore, the angle as measured is relatively free from the large errors due to the liquid advancing or receding from the solid. Added advantage can be obtained by placing the jar in a small outer tray with a draining tube so that by providing a suitable source of supply,

pure water can be run continually into the jar J and overflow at the level of the line of contact so that the surface is automatically swept and renewed.

The jar J is a rectangular one, preferably with plate glass sides front and rear, such as an absorption cell for photometric work. A glass is ruled with black lines at intervals of about 3 mm. and is cemented to the rear surface. In place of this, a single fine black wire, held around the jar by means of a rubber band on one side, may be used. A small mirror is placed in front of the jar J at an angle. The height of the liquid is so adjusted that it is just up to the axis of rotation. The slide S is then tilted until the image of the straight lines, seen in the mirror, reflected from the under side of the liquid-air interface, appears perfectly straight right up to the line of contact. To facilitate this a ground glass and suitably bright electric lamp are placed on the far side of the jar.

The substances used throughout were Eastman Synthetic Organic Chemicals and of as high purity as is commercially obtainable. In several cases these were recrystallized. A sample of the substance to be used was melted in a small test tube and several drops allowed to crystallize on the end of a clean microscope slide.

Great precautions, of course, had to be taken to assure the cleanliness of all the glassware used and the purity of the water. Potassium dichromate cleaning solution was used on the glassware and the surface tension of the water was checked before every determination. This was done at first by means of a du Noy tensiometer. It was found, however, that this could be done more conveniently and just as accurately by placing a slide of pure paraffin of known contact angle in the apparatus and reading the angle. A very slight difference of surface tension or contamination of any sort could be very easily detected by the lowering of the angle.

As previously inferred, the Ablett cylinder and the plate methods gave many widely divergent results, the cause of which is unknown and requires further investigation. Some of these discrepancies are shown in Table I.

TABLE I
Comparison of Contact Angle measured by Ablett Cylinder and by Plate Methods

| | Cylinder | | Plate |
|---------------------------|----------|----|-------|
| | Out | In | |
| Myristic acid | 60 | — | 115 |
| Palmitic " | 54 | 36 | 111 |
| Stearic " | 53 | 91 | 106 |
| Ethylene glycol dilaurate | 76 | 94 | 123 |
| " " distearate | 56 | 64 | 75 |
| Cellulose acetate | 58 | — | 25 |
| " nitrate | 77 | — | 15 |
| 2-4-6 trichlor aniline | 62 | 90 | 55 |

While in none of these measurements by either method was the surface of the water swept, it is to be noted that several of the above substances do not contaminate a water surface in the ordinary sense (lower the surface tension). Ethylene glycol dilaurate and distearate, and stearic acid, do not affect the surface tension. Because of erratic results obtained in a few cases with the cylinder, and because of the greater convenience and ease of measurement with the plate method, as well as the general consistency of the results obtained, the latter has been preferred for the present at least, and the measurements discussed below were all made in that way.

By use of overflow at the surface with the plate method as already suggested, the surface is swept continually, and if this is desired, the apparatus as illustrated is most convenient. However, unless contamination from a foreign substance is considered, and this is not likely under ordinary conditions of cleanliness, there is no particular advantage in sweeping the surface. Even though the material under examination lowers the surface tension by a large amount, the values of T and θ in the equation $W = T(1 + \cos \theta)$ are those under such conditions. As long as the solid is in contact with water, at any rate, sweeping will have no noticeable effect on the observed surface tension, unless, of course, the rate of solution is extraordinarily slow. If any foreign substance, however, is present, this will be swept away.

The plate method is more susceptible to foreign contamination than the cylinder. For example, pure paraffin was coated on a cylinder and turned on a lathe to give a smooth surface, and the same material was coated on a slide and scraped. The contact angle measured by the two methods with these specimens was in each case 108° . A very small fragment of cetyl alcohol was then dropped on the water in each case. Cetyl alcohol lowers the surface tension of water 50%. The contact angle was lowered from 108° to 96° with the cylinder method, and from 108° to 72° with the plate. No reason is known for this difference between the two methods.

Another objection to the cylinder method is the difficulty of measuring small angles. Unless the top surface of the water-air interface is used for reflection, and this is poor, giving a very faint image, the angle cannot be determined if it is much under 60° . Since many substances give angles from 30° to 60° measurements on them are best made by the plate method.

Results

Measurements here recorded for solids are, within limits of error, well in accord with other similar work for liquids and the more limited published results for solids. Harkins and his co-workers¹ have demonstrated quite clearly the existence of certain polar groups and their effect on the work of adhesion of liquids, as measured by the method of interfacial tension. Langmuir² has also put forth views which have experimental verification and which explain the effects of polar groups in producing molecular orientation.

¹ J. Am. Chem. Soc., 39, 354 (1917); 42, 700 (1920); 43, 35 (1921).

² J. Am. Chem. Soc., 39, 1848 (1917); Chem. Met. Eng., 15, 468 (1916).

That the measurement for solids are comparable with results of Harkins for liquids is fairly well indicated by Table II. Comparisons are made for the substances of similar constitution which could be found in the measurements by the two methods. The results for liquids are calculated from the values of the surface tensions of the two liquids and the interfacial tension. Those for solids are based on the measurement of contact angle and surface tension of water in contact with solid.

TABLE II

| Liquids (Harkins) | | Solids (Niets) | |
|---------------------------------------------|-------|------------------------------------|-------|
| Paraffin Oil | 47.8 | Pure paraffin | 49.9 |
| Benzene | 66.5 | Benzene, solid at 1° | 43.5 |
| Ethyl ether | 79.2 | Diphenyl ether | 77.2 |
| Isobutyl alcohol | 94.3 | Trichlorotertiary butyl alcohol | 102.9 |
| Cyclohexanol | 103.7 | Triphenyl carbinol | 111.7 |
| Methyl hexyl carbinol | 99.7 | Methyl cinnamate | 111.0 |
| Ethyl cinnamate | 89.9 | Caprylic acid | 66.2 |
| Caprylic acid | 93.72 | Undecylenic acid | 70.0 |
| Undecylenic acid | 102.7 | Diphenyl amine | 85.4 |
| Di-isobutyl amine | 84.56 | | |
| $((\text{CH}_3)_2\text{CHCH}_2)_2\text{NH}$ | | | |
| Dipropyl amine | 93.68 | | |
| $(\text{C}_3\text{H}_7)_2\text{NH}$ | | | |
| Chlorobenzene | 68.46 | 1-2-4 trichlorobenzene | 62.6 |

TABLE III

Values of Work of Adhesion—Liquid Phase

| Paraffins | Harkins, Clark and Roberts: J. Am. Chem. Soc., 42, 700 (1920) |
|------------------------------------------------------------------|------------------------------------------------------------------|
| Isopentane $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$ | 36.88 |
| Hexane | 39.98 |
| Octane | 43.76 |
| Di-iso butyl (decane) | 48.24 |
| Higher paraffins (about $\text{C}_{16}\text{H}_{34}$) | 63.02 |
| Aromatic Hydrocarbons | |
| Benzene | 66.62 |
| Toluene | 66.62 |
| o-xylene | 66.62 |
| m-xylene | 63.62 |
| p-xylene | 63.36 |
| Ethyl benzene $(\text{C}_6\text{H}_5(\text{CH}_2)_2)$ mesitylene | 63.36 |
| p-cymene | 60.48 |

TABLE IV
General Data on Work of Adhesion

| | 1 | 2 | 3 | 4 | 5 |
|-----------------------------|-----|-----|-----|----|-------|
| Hydrocarbons | | | | | |
| Hydrocarbons | | | | | |
| Dibenzyl | 50 | 0 | 0 | M | 118.8 |
| Stilbene | 72 | 0 | 0 | MS | 94.7 |
| Diphenyl | 68 | 0 | 0 | MS | 99.6 |
| Paraffin | 108 | 0 | 0 | N | 49.9 |
| Benzene | 105 | 22 | 9 | V- | 43.5 |
| Naphthalene | 62 | 0 | 0 | N | 106.3 |
| Anthracene | 92 | 0 | 0 | NS | 68.6 |
| Diphenyl methane | 62 | 3 | 4 | M+ | 103.6 |
| Triphenyl methane | 45 | 0 | 0 | N | 123.4 |
| Tetraphenyl methane | 15 | — | — | — | 135.0 |
| Ethers | | | | | |
| Glyceryl phenyl | 51 | 17 | 8 | V+ | 97.6 |
| Diphenyl | 88 | 0 | 9.2 | S | 75.7 |
| Alcohols | | | | | |
| Myristil | 60 | 50 | 50 | V- | 54.2 |
| Cetyl | 46 | 50 | 50 | MV | 61.3 |
| Menthol | 73 | 23 | 22 | V | 71.8 |
| Trichloro tert. butyl | 65 | 13 | 7 | V+ | 102.9 |
| Triphenyl carbinol | 57 | 0 | 0 | N | 111.7 |
| Aldehydes | | | | | |
| Trioxymethylene | 122 | 0 | 7 | N | 34.5 |
| p-iso-butyraldehyde | 70 | 22 | 17 | V | 75.6 |
| Ketones | | | | | |
| Acetophenone | 65 | 19 | 0 | V | 83.4 |
| Benzophenone | 65 | 2.8 | 11 | MV | 100.0 |
| Phenols | | | | | |
| β -naphthol | 35 | 11 | 12 | M | 128.5 |
| Resorcinol | 25 | 0 | 6 | V | 137.8 |
| Thymol | 85 | 17 | 28 | VM | 65.6 |
| Amines-Amides | | | | | |
| Diphenyl amine | 80 | 0 | 5 | SN | 85.4 |
| 2-4-6 trichloro aniline | 55 | 0 | 0 | N | 114.5 |
| Acetamide | 15 | 4 | 12 | V | 143.0 |
| Halide Substitutions | | | | | |
| 1-2-4 trichloro benzene | 98 | 0 | 0 | SN | 62.6 |

TABLE IV (Continued)
General Data on Work of Adhesion

| | 1 | 2 | 3 | 4 | 5 |
|-----------------------------|-----|-----|------|----|-------|
| Hydrocarbons | | | | | |
| Nitrogen Cpds. | | | | | |
| Azobenzene | 64 | 0 | 0 | N | 104.5 |
| Hydrazobenzene | 52 | 1.1 | 2.8 | N | 118.7 |
| Acids | | | | | |
| Caproic | 45 | 30 | — | — | 87.0 |
| Caprylic | 60 | 38 | — | — | 66.2 |
| Pelargonic α | 49 | 45 | — | — | 66.1 |
| " β | 69 | 45 | — | — | 54.0 |
| Capric | 85 | 43 | — | — | 45.1 |
| Undecylic | 79 | 44 | — | — | 50.8 |
| Lauric | 111 | 31 | — | — | 32.6 |
| Tridecylic α | 75 | 45 | — | — | 50.4 |
| " β | 95 | 40 | — | — | 36.5 |
| Myristic | 115 | 25 | — | — | 32.0 |
| Pentadecylic α | 73 | 31 | — | — | 65.0 |
| " β | 110 | 21 | — | — | 37.8 |
| Palmitic | 111 | 6 | — | — | 42.8 |
| Margaric α | 77 | 0 | — | — | 80.0 |
| " β | 105 | 9 | — | — | 54.2 |
| Stearic | 106 | 0 | — | — | 56.8 |
| Arachidic | 111 | 0 | 0 | N | 46.7 |
| Behenic | 110 | 0 | 0 | N | 47.9 |
| Cerotic | 116 | 0 | 0 | N | 40.8 |
| Erucic | 93 | 33 | 10 | M | 46.2 |
| Cinnamic | 40 | 0 | 3.7 | MS | 127.7 |
| Hydrocinnamic | 63 | 17 | 17 | MV | 87.2 |
| Undecylenic | 53 | 40 | — | — | 70.0 |
| Benzoic | 65 | 9.5 | 2.8 | V+ | 93.6 |
| Esters | | | | | |
| Methyl cinnamate | 45 | 10 | 15.7 | V- | 111.0 |
| Ethylene glycol dicaprylate | 84 | 14 | — | — | 68.8 |
| " " dicaprinate | 96 | 8 | — | — | 59.5 |
| " " dilaurate | 123 | 0 | — | — | 32.8 |
| " " dimyristate | 110 | 0 | — | — | 47.6 |
| " " dipalmitate | 98 | 0 | — | — | 62.2 |
| " " distearate | 75 | 0 | — | — | 91.1 |
| Butyl carbamate | 40 | 26 | 1.9 | V+ | 95.1 |
| Tristearin | 110 | 0 | 0 | N | 47.0 |
| Miscellaneous | | | | | |
| Benzyl sulfide | 90 | 0 | 1 | N | 72.8 |
| Zinc stearate | 135 | 0 | +5 | S | 21.3 |
| Castile soap powdered | 68 | 65 | 53 | MV | — |

In the case of benzene, caprylic acid, and undecylenic acid, measurements were made on both liquid and solid and in each case values for the liquid are higher. The general trend of the results for solids closely parallels those for liquids, however. Measurements of a series of solid homologues, or of solid compounds with similar terminal groups, show greater variations within the group than for a similar class in Harkins' data for liquids. This is seen by comparison of Table IV with some of Harkins' values for related compounds. In Table III are given a few of the latter for hydrocarbons, which as a whole show far less divergence than the hydrocarbons, in Table IV.

Table IV gives complete data on contact angle and work of adhesion for 70 organic solids. Values given are for the following:

| | |
|----------|--------------------------------------------------------------|
| Column 1 | Contact angle, θ |
| Column 2 | % reduction of the surface tension of water caused, T_R |
| Column 3 | % reduction of the contact angle of pure paraffin θ_R |
| Column 4 | notes on spreading |
| Column 5 | Work of adhesion, W |

Column 2 is expressed as a percentage and represents the lowering of surface tension of water in the presence of solid. Column 3 shows the percentage lowering of the contact angle of pure paraffin against water in the presence of the solid in question.

The data on spreading are only roughly quantitative and are expressed as

V violent
M moderate
S slight
N none

It is at once evident from Table IV that in each chemical class there is a rather wide range of values for the work of adhesion, W . There is also no tendency for any class to assume a particular value. This indicates of course that other factors than the mere presence of the better known polar groups influence the attraction for water. It is unfortunate that it is difficult to secure more comparisons, as can be done for liquids, between series of related compounds. Many of the substances needed are not solid at ordinary temperatures, and a great many are very difficult to prepare in any state of purity. Consequently, it will require time to secure even a moderate amount of data. Nevertheless, the figures of Table IV afford some interesting information.

Discussion for the present will be confined to work of adhesion only. Following are some of the comparisons which may be found in the table.

| | |
|--------------|------|
| Benzene | 43.5 |
| Benzoic Acid | 93.6 |

The carboxyl group causes a great increase in the work of adhesion, as expected. The measurements for benzene were made in the solid state, in water at 1°.

| | |
|-------------------|-------|
| Naphthalene | 106.3 |
| β -Naphthol | 128.5 |

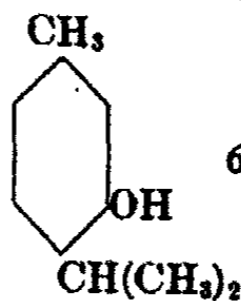
The increase here is appreciable, though not large. A single phenolic hydroxyl group on the large naphthalene molecule already containing polar double bonds would probably not be able to exert much effect.

Two phenolic groups in the benzene ring, however, produce a very great change.

| | |
|-----------------------|-------|
| Benzene | 43.5 |
| Resorcinol (1:3OH) | 137.8 |

A single phenolic group with an additional methyl group in thymol produces only a moderate increase.

| | |
|---------|------|
| Benzene | 43.5 |
| Thymol | 65.5 |



The -Cl radicle is shown as polar from the values for trichlorobenzene.

| | |
|------------------------|------|
| Benzene | 43.5 |
| 1-2-4 trichlorobenzene | 62.6 |

The alcoholic hydroxyl appears to have greater attraction for water than the carboxyl group. This is at least the case for two of the higher hydrocarbons, as shown by

| | | | |
|------------------|------|---------------|------|
| Myristyl alcohol | 54.2 | Cetyl alcohol | 61.3 |
| Myristic acid | 32.0 | Palmitic acid | 42.8 |

These values are put forward with reserve, since they seem inconsistent and these higher solid alcohols are purified with difficulty.

The effect of additional polar groups is again seen in values for two ethers.

| | | |
|-----------------------|------------------------------------------------------------------------------|------|
| Glycerol phenyl ether | $\text{CH}_2\text{OH}.\text{CH}(\text{OH}).\text{CH}_2\text{OC}_6\text{H}_5$ | 97.6 |
| Diphenyl ether | $\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$ | 75.7 |

Some interesting results are afforded by the following measurements on substituted methanes. The value for toluene is taken from Harkins' results for liquids but is inserted for comparison.

| | |
|--------------------------|-------|
| Benzene (solid) | 43.5 |
| Toluene (liquid-Harkins) | 66.6 |
| Diphenyl methane | 103.6 |
| Triphenyl " | 123.4 |
| Tetraphenyl " | 140.0 |

The last value for tetraphenyl methane is not exact, the result lying between 140.0 and 145.6. The tetraphenyl methane was very kindly furnished by Dr. Edward Mack, Jr.

The differences between each member and the next of this series are

| |
|-------------------|
| Benzene |
| 23.1 |
| Toluene* |
| 37.0 |
| Diphenyl methane* |
| 19.8 |
| Triphenyl " |
| 16.6 |
| Tetraphenyl " |

These indicate roughly a steady constant increase for each phenyl group added, the increase becoming less as the molecule becomes larger. They also show again the effect of the double bonds of the benzene ring.

The di- and tri-phenyl methanes show a result on cooling in contact with water which is not understood at present, it being mentioned only as a matter of record. This peculiar effect is illustrated by the following:

| | Cooled in Air | Cooled in Contact with Water |
|------------------------------------|---------------------------|---------------------------------|
| Diphenyl methane | { θ 62° W 104 | 93° 67 |
| Triphenyl methane | { θ 46° W 123.4 | 153° 7.9 |
| Stearic acid (See Table V also) | { θ 106° W 52.8 | 96° 65.2 |

The substituted methanes give results in the opposite sense from most substances cooled in contact with water, as, for example, stearic acid. That is, instead of the water producing increased work of adhesion through orientation of polar groups, it has produced less. In the case of triphenyl methane especially the change is tremendous, work of adhesion being reduced to approximately one-fifteenth by cooling on water. Conditions causing results in this direction might be the leaching-out of a very highly polar impurity, which we believe improbable, or an adsorption effect. At any rate we have not yet been able to investigate the matter further.

Other results with aromatic hydrocarbons are the following:

| | |
|-------------|-------|
| Benzene | 43.5 |
| Naphthalene | 106.3 |
| Anthracene | 68.6 |

The increase from benzene to naphthalene is seemingly accounted for by the addition of the second nucleus and the double bonds it contains. The decrease shown by anthracene over naphthalene might be explained by assuming some sort of folded configuration for the naphthalene molecule, but this is not borne out by the findings of Bragg¹ as to the x-ray crystal structure.

*The value for toluene is out of line, since, as previously stated, a liquid gives a higher result than the same substance in solid form.

¹ Proc. Phys. Soc., 34, 33 (1921); 35, 167 (1923).

Consequently we are again confronted by facts difficult to explain. It seems possible that in some of these cases consideration should be given to the structure of the crystal aggregate rather than to the individual molecule alone.

Another case in which configuration may play a part is:

| | |
|-------------|-------|
| Diphenyl | 99.6 |
| Naphthalene | 113.7 |

Mack¹ has shown that diphenyl has a "collapsed" or folded structure. The molecule consists of two benzene nuclei face to face. Consequently the residual valences are probably quite completely satisfied within the molecule itself. Naphthalene has a more extended configuration, and four of the double bonds are effective in increasing the work of adhesion.

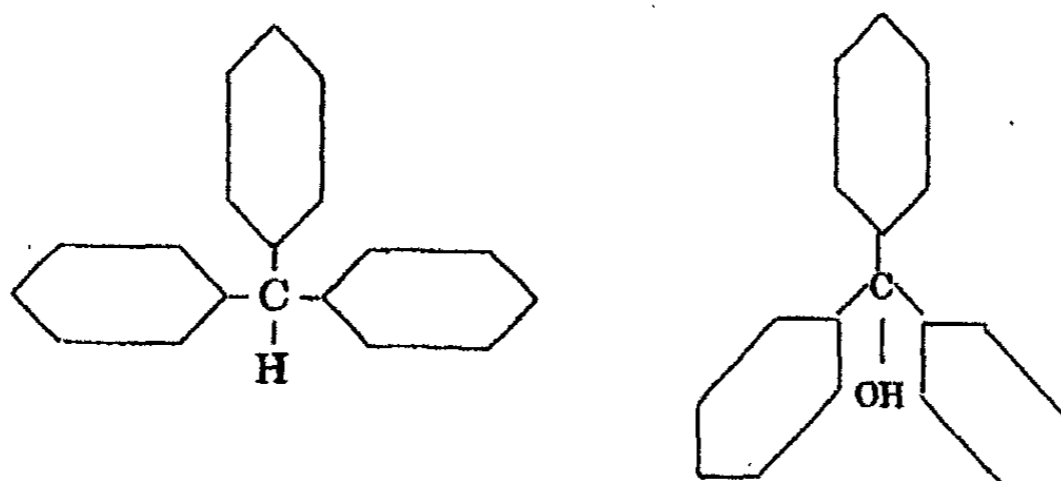


FIG. 4

A comparison offering further difficulties is the following:

| | |
|--------------|-------|
| Diphenyl | 99.6 |
| " ether | 75.7 |
| Benzophenone | 100.0 |

These results have been repeated and verified, though absolute values cannot be duplicated as a rule. The decrease from diphenyl to the ether must be due to a change in configuration of the molecule caused by the introduction of the oxygen atom. If this is the explanation, we are not able to describe the nature of the change as yet. The increase from the ether to the ketone is rather marked, but further data are required before any conclusions can be drawn. This increase is probably analogous to the increase in solubility in water of acetone over ether.

A comparison which at present seems to offer some difficulties in the way of satisfactory explanation is

| | |
|--------------------------------------------------------------------|-------|
| Triphenyl methane (C ₆ H ₅) ₃ CH | 123.4 |
| " carbinol (C ₆ H ₅) ₃ COH | 111.7 |

It would seem very difficult to explain the higher value for the hydrocarbon, unless we should go so far as to assume that by means of steric hindrance

¹ J. Am. Chem. Soc., 47, 2468 (1925).

the hydroxyl of the carbinol is prevented from exercising any effect. This would be the case if we had a configuration such as shown in Fig. 4. Any such explanation must of course be put forward with reserve, and requires additional evidence.

Some information concerning the effect of double bonds is available from Table IV. Below are tabulated the values for six pairs, the double-bonded compound being the second in each case.

| | | | |
|----------------------|-------|-----------------|-------|
| Undecylic acid | 50.8 | Behenic acid | 47.9 |
| Undecylenic acid | 70.0 | Erucic acid | 46.2 |
| Hydrocinnamic acid | 87.2 | Hydrazo benzene | 118.7 |
| Cinnamic " | 127.7 | Azo benzene | 104.5 |
| Stearic acid | 56.8 | Dibenzyl | 118.8 |
| Oleic acid (Harkins) | 89.62 | Stilbene | 94.7 |

In the first three cases the increase due to the double bond is considerable. In the last three there is a decrease. This would seem to fit in with the theory proposed a short time ago by T. M. Lowry¹ that double bonds are of two kinds. The first he calls the non-polar, and the second the semi-polar. The non-polar bond consists of two co-valences and the semi-polar of one co-valence and one electro-valence. At any rate we should feel quite safe in saying that there is a wide distinction between the double bonds of the first three and of the last three pairs. Just why any such bond should show what is apparently a decrease over the saturated compound is not clear. It is hoped that later evidence will throw light on the matter.

Spreading

The spreading of substances, particularly solids on liquids, as shown by the well-known case of camphor particles placed on water, has long been the subject of speculation. A complete and satisfactory explanation is however lacking. Various theories have been proposed, most of which have been associated with the effect of substances that spread on the surface tension of the liquid. It seems likely that this explanation is not sufficient for in certain cases of violent spreading the reduction of surface tension is very slight and other factors such as solubility and volatility affect the spreading. Trichloro tertiary butyl alcohol serves as a good example of some of these effects. When a small amount is first added to water the surface tension seems unaffected. After a few minutes the surface tension is gradually lowered until after about a half hour the decrease may amount to as much as 13%, depending on conditions. If the experiment is conducted in a small vessel which may be closed air tight, it will be found that as long as relatively small amounts are used and the vessel left open, violent motion will continue. If much larger amounts of solid are used, motion will cease as the water becomes saturated, or it will also stop if the cover is put on and the air becomes saturated (apparently) with the vapor of the substance. In the latter case slight motion is resumed

¹ Lowry: J. Chem. Soc., 123, 822 (1923); Bull., 39, 203 (1926).

if the cover is again removed, though the degree of motion is very much less than before. Consequently, it seems certain that solubility, and to a much less extent, volatility, are factors in spreading.

Table IV does not contain sufficient data to warrant any conclusions, since it shows only that in most cases of spreading the surface tension is lowered. Substances which show no spreading do not reduce the surface tension. The violence of spreading does not seem to be proportional to the surface tension lowering.

Effect on Orientation of Conditions during Crystallization

While a substance is crystallizing, heat and humidity have a large influence in determining the nature of the exterior face of the solid; in fact it is for this one reason, if for no other, that different samples of the same substance give different values. To insure reproducibility would require careful control of conditions during crystallization. It is rather surprising, in a way, that even in the solid phase some molecules are able to turn with such ease and to present an oriented arrangement. These facts are illustrated rather nicely by Table V which is practically self-explanatory, representing a series of experiments in which the humidity was varied considerably. The work of adhesion for stearic acid varies from 39.7 where crystallization took place in perfectly dry air at low pressure, to 131.0 when crystallization occurred in air saturated with steam at about 35°. Experiments G, H, J and K show that

TABLE V
Effect of Conditions during Crystallization on Orientation

| | Stearic Acid | Capric Acid |
|--------------------------------------------------------------------------------|--------------|-----------------|
| A. Cooled in vacuum desiccator at 15-20 mm. over P ₂ O ₅ | W = 39.7 | W = 58.4 |
| B. Cryst. in Lab. air at 23° Ordinary humidity | 54.0 | 58.4 |
| C. Cryst. 2 ft. from escaping steam | 65.2 | 52.2 |
| D. Cryst. 1 ft. from escaping steam | 80.2 | |
| E. Cryst. in cloud of steam and read immediately | 104.5 | |
| F. Cryst. in cloud of steam, Value 2 min. Apparently steady. | 131.0 | 71.2 |
| G. Samples cooled in desiccator, then in contact with water, after 2 1/2 hrs. | 111.2 | 71.2 |
| H. Samples cooled in desiccator, then in contact with water, after 24 hrs. | 74.2 | 70.8 |
| J. Sample cooled in desiccator left in Lab. air at 23°—2 1/2 hrs. | 75.3 | |
| " " " 24 hrs. | 70.3 | |
| K. Sample cooled in desiccator and read at intervals after immersion in water | 67.7 | 0 minutes 58.4 |
| | 88.0 | 15 minutes 61.6 |
| | | 3 hours 61.0 |
| L. Cryst. in contact with water 4/2/27 | 70.3 | |
| 11/19/26- | 65.2 | 77.4 |

samples crystallized as in A, after immersion in water at ordinary room temperature for some time, even after comparatively short times (15 min. in K) show increased work of adhesion, i.e., increased orientation of polar groups toward the water. This process therefore seems to occur with comparative ease. Experiments B, C, D and E show the effect of increasing humidity while crystallization is taking place.

We are as yet at a loss to explain the great difference between experiments E and L for stearic acid where crystallization occurred in steam and on water.

Conclusions

1. A preliminary study has been made of two principal methods of measuring contact angle. These are

- (a) the Ablett cylinder
- (b) the plate method

The first of these is considered more or less uncertain at present, since it shows mysterious, unexplainable, and inconsistent results compared with the plate method.

2. About 70 organic substances have been studied for contact angle, effect on surface tension of water, spreading, and work of adhesion. The results, in all cases, appear to be in accord with other results on liquids and solids and with theories proposed by Harkins and Langmuir.

3. Some evidence on spreading is given. It is shown that some substances which spread violently do not affect the surface tension very greatly. Substances which do not spread do not lower the surface tension.

4. The effect of humidity during crystallization is very marked. Increased humidity while solidification takes place causes great increase in work of adhesion. Increase in number of polar groups exposed to water also occurs if the solid is immersed in water.

*Rochester, N. Y.,
July 1, 1927.*

THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN IODIDE; THE MODE OF OPTICAL DISSOCIATION¹

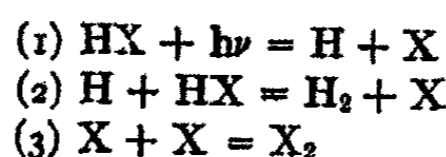
BY BERNARD LEWIS²

Introduction

Part I. Kinetic

The problem of determining by direct experiment the true mechanism of the photochemical decomposition of hydrogen-bromide or hydrogen-iodide studied by Warburg³ is of no little interest and importance since such knowledge would afford information concerning the conditions under which a molecule decomposes after it has become activated as a result of absorption of radiation.

It will be recalled that Warburg suggested the following steps in the decomposition after a thermodynamic consideration of the possible occurrence of secondary "dark" reactions:

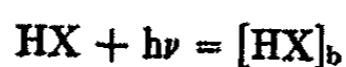


where X denotes the halogen atom.⁴ This accounts exactly for the experimentally determined quantum efficiency of two molecules decomposed for each quantum of energy absorbed. Stern and Volmer⁵ have presented an entirely different point of view which does not violate the observed quantum efficiency. They argue that in this type of reaction a collision is necessary between the active molecule and some other molecule during the mean life of the active state before decomposition can take place and they conclude that the hypothesis that molecular dissociation or decomposition is the primary light process, cannot be entertained. Some of the bases of their arguments have since been found to be untenable. For instance, assuming the heat of dissociation of Cl₂ as 106,000 calories they pointed out the impossibility of a direct splitting of the chlorine molecule into atoms as a result of absorption of radiation since the energy available in the spectral region in which the combination of hydrogen-chloride occurs, namely about $\lambda = 4000\text{A}$, ($Nh\nu = 71,300$ calories) is considerably less than the heat of dissociation of chlorine. A collision therefore seemed necessary to meet the added energy requirement. This must now be ruled out since the heat of dissociation of Cl₂ as more recently determined kinetically⁶ and spectroscopically⁷ is 54,000 — 58,000 calories. Thus there is sufficient energy available in the quantum. That Cl₂ does dissociate in a single and elementary act by absorption of radiation in this region will be evident from spectroscopic considerations presented in Part II of this introduction.

It is true, however, that experiments on gas fluorescence⁸ and on the excitation of molecular spectra by electron impact⁹ show that at low pressure a

molecule may absorb many times its dissociation energy without dissociating. For example, iodine, whose heat of dissociation is 34,500 calories⁶ can absorb and emit as a resonance spectrum, an amount of energy five times the work of dissociation, when illuminated by the line $\lambda = 1849\text{\AA}$.¹⁰ Again a hydrogen molecule excited by electron collision can emit as molecular spectrum several times the amount of the dissociation energy. From the excitation of x-ray spectra, values of the excitation energy can be evaluated which may exceed the work of dissociation a thousand times without leading to dissociation by a primary process. The explanation of this effect seems to be found in the primary employment of the excitation energy in raising the electron system to a higher quantum state, while the oscillation and rotation energies are only altered by the coupling of their periods with those of the electron system.¹¹ Another plausible explanation, more applicable to complex molecules, is that, under certain conditions, there may be a finite interval between the absorption of energy and the decomposition of the molecule, since the former may not be distributed at once in the particular manner necessary for dissociation. During this interval a collision or some other disturbing factor may cause the emission of the energy as radiation.

Conceiving the primary light process as resulting in an energy-rich modification of the molecule, which, on the Bohr conception would be a molecule with an electron in an orbit farther removed from the nucleus, Stern and Volmer prefer to write

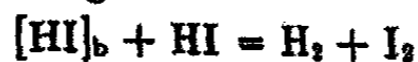


where $[\text{HX}]_b$ indicates the active state. In order to suit its condition to its surplus energy the active molecule requires a collision with another molecule before it can decompose,



the steps of which may be several and of the type proposed by Warburg in his thermodynamic treatment.¹² According to these authors this will occur provided the active molecule suffers a collision during its term of life, viz., ca. 10^{-7} sec. which has always been the case in the concentrations hitherto investigated. (Warburg worked at pressures of HI ranging from 80 m.m. to 350 m.m.). Otherwise the energy will be radiated or dissipated as kinetic energy. With inert gases or hydrogen present a small portion of the energy may be transferred to the foreign gas at each collision, the excited HI molecule taking up new and successive rotational quantum states, which, according to Stern and Volmer, seems possible with halogen-hydrides judging from their rather complicated infra-red spectrum. A sufficient number of successive collisions with a foreign gas may finally result in the deactivation of the $[\text{HX}]_b$ molecule. This would of course presuppose a relatively long life for the active state which is not inconceivable for rotational quantum jumps as the calculations of Tolman¹³ show. The decomposition of HBr and HI was studied by Warburg in the presence of N_2 and H_2 . Neither here nor when HI was mixed

with 0, 1 or $2\frac{1}{2}$ atmospheres of N_2 ¹⁴ was the decomposition affected in the least, the quantum efficiency still remaining two. This does not exclude the possibility of the reaction taking the course



since $[HI]_b$ evidently may keep its energy after a collision with certain molecules. It is a fact now coming to light that active molecules show varying susceptibilities to change on collision with different foreign gases.¹⁴

Bodenstein¹⁵ concluded that the photochemical decomposition of HI is unimolecular and Trautz and Scheifele¹⁶ reach the same conclusion for the early stages of the reaction. This does not signify that collisions are unnecessary since the decomposition may still be unimolecular with respect to the active molecules as presented in a mechanism above.¹³

From a kinetic point of view probably the most direct method which will enable one to determine whether the excited molecule may decompose without the stimulus of a collision, is to study the quantum efficiency at sufficiently low pressures of pure gas so that a molecule of HI, activated by absorbed radiation, is unable to make a collision with an ordinary HI molecule before its mean free life, viz., 10^{-7} sec.¹⁷ has terminated or before it decomposes of its own accord. In the former case if reversion takes place i.e. if a molecular encounter is a condition which must be fulfilled for decomposition, one would expect the quantum efficiency to be small. In the latter case if the molecule decomposes in a single act, the quantum efficiency should remain two as at high pressures. The results are markedly different and it should not be difficult to distinguish between these two alternatives. Accordingly, the present paper contains an account of these experiments in full.

Part II. Spectroscopic

Since the writer purposed studying this reaction, spectroscopic data¹⁸ of considerable importance have been published on which the results of these experiments have direct bearing.

Franck¹¹ pointed out that molecules which are bound together by van der Waals' forces such as the halogens can be separated into atoms by an adiabatic process and that illumination with radiation of the proper wave-length may cause dissociation into normal and excited atoms in a single act. The considerations due to Franck leading to this conclusion will be given in brief. Whether a photochemical dissociation is possible in an elementary act is dependent on the magnitude of the changes in oscillation and rotation energies which are coupled with changes in the electron system on absorption of light. Dissociation can take place when this change equals the energy of dissociation for the state considered. In the absorption spectrum a band convergence limit appears whenever the binding energy of the unexcited molecule in the lowest oscillation quantum state is changed by a suitable amount by transition of the electron system to a new quantum state due to absorption of light. Since the electron jump occurs so quickly that the heavy atoms maintain their relative position to each other during the transition period, potential energy is conveyed to the nucleus due to the electron jump. This

potential energy is dependent on the change in binding. With strong changes in binding, the potential energy is greater than the work of dissociation for the excited state and the molecule dissociates. By exchange of potential to kinetic energy the molecules break up with kinetic energy and instead of a band spectrum a continuous spectrum appears whose maximum is often displaced away from the convergence limit toward shorter wave-lengths. With iodine⁷ the change in binding is so great that the maximum absorption is found in the neighborhood of the convergence limit whereas with chlorine⁷ it is displaced considerably in the continuum toward shorter wave-lengths. It is concluded that the absorption of light of wave-length equal to or shorter than this limit ($\lambda = 4995\text{\AA}$ for I_2 ; $\lambda = 4785\text{\AA}$ for Cl_2) will lead to dissociation of non-polar molecules in an elementary act.

The earlier views of Franck have been amplified and clarified recently.¹⁰ F. Hund²⁰ has shown that the processes involved in the transition of an electron from the system of the anion to that of the cation are indicated from the principles of quantum mechanics. The process of decomposition in an elementary act by absorption of radiation can now be extended to polar molecules. Kondratjew²¹ has presented what seems to be conclusive experimental evidence that sodium-iodide may so decompose into a normal I atom and an excited Na atom.²² He finds that at 10^{-3} m.m. Hg the sodium D lines are emitted in a sharply defined beam whose dimensions are given by the boundary of the exciting cone of light. If a collision were necessary to disrupt the NaI molecule the excited molecule could have moved several centimeters (mean free path ca. 5 cms.) outside the zone before suffering a collision and the fluorescence would have been located far removed from the cone of exciting radiation. Furthermore, Kondratjew found that the fluorescence is proportional to the first power of the pressure²³ which seems unequivocally to signify that NaI decomposes in an elementary act by absorption of radiation. Terenin²⁴ showed that all wave-lengths below $\lambda = 2500 \text{\AA}$ give rise to the emission of the sodium D lines in NaI vapor indicating that NaI should absorb continuously in this region, which Franck, Kuhn and Rollefson have shown to be the case.¹⁹

It would appear further from the work of Franck, Kuhn and Rollefson and Franck and Kuhn²⁵ that although HI, possessing infra-red rotation-oscillation absorption spectra and a small dipole electric moment, is considered polar in character, its atoms are not bound by the same type of forces as exist in the alkali-halides. The latter are characterized as "ion-linkages" where the forces exist between ions and the HI molecule as an "atom-linkage" where the forces exist between the nuclei, the criterion being the constituent parts into which the molecule decomposes. The view that the halogen-hydrides possess a different type of binding than the alkali-halides is strengthened not only by the criterion set up by these authors for their distinction but also by the work of Bell.²⁶ From a determination of the constants of the equation of the infra-red absorption bands of the halogen-hydrides, Bell was able to evaluate the variation with distance of the force acting on the hydrogen nucleus as it vibrates along the line joining the two nuclei. The results show that the

hydrogen nucleus is within the halogen electron shell and is buried to the same depth in all. If this is the case, then the union of a hydrogen atom with an iodine atom consists of a transfer of the hydrogen electron to complete the iodine shell and the penetration of the hydrogen nucleus within the iodine electron shell.²⁷ One would hardly expect the binding force to be ionic in character but rather as one between the nuclei. In fact it has been shown²⁸ that the lattice structure of HCl is atomic and not ionic. Indeed from these facts as well as both the character of the continuous absorption spectrum and its mode of decomposition one might consider HI as more nearly approximating to a non-polar than to a polar molecule despite its display of infra-red spectra and a small dipole electric moment.

Both Tingey and Gerke¹⁸ and Bonhoeffer and Steiner¹⁸ believe the continuous absorption of hydrogen-iodide to be sufficient evidence to eliminate Stern and Volmer's mechanism and to be consistent with Warburg's mechanism. However, direct experimental proof that a primary decomposition can occur without a collision is desirable, especially since the character of the absorption spectrum of HI is different from that of non-polar and strictly polar molecules such as NaI, no band convergence nor maxima in the continuum being observed.

Determination of the Experimental Pressure of HI to be employed in the present investigation and the probability of collision of an active molecule

Assuming in agreement with known data, that the mean life of a molecule in its electronic excited state is of the order 10^{-7} sec., one may calculate the gas pressure at which on the average a collision will not occur during this time interval. From the kinetic theory the number of collisions per second between an active HI molecule and any other HI molecule²⁹ is given by

$$Z = 2\sigma^2 n_1 \sqrt{2\pi kT} / m \quad (1)$$

where n_1 is the number of molecules of HI per c.c.

m is the mass of an HI molecule.

T " " absolute temperature.

σ " " sum of the radii of the participating molecules or the mean distance of approach of their centers.

k is the Boltzmann constant.

$$n_1 = p N / RT \quad 1333.3 \quad (2)$$

where p is the partial pressure of HI in m.m. Hg.

N is the no. of molecules per gram mol.

From this it follows that

$$Z = \sigma^2 p \quad 5333.2 \sqrt{\frac{\pi N}{kTM}} \quad (3)$$

where $k = R/N$

The expression $T = l / \bar{u} = 1/Z$, where l is the mean free path and \bar{u} the root mean square velocity, gives the mean time between collisions or the duration of a mean free path.

$$1/Z = T = 1/\sigma^2 p A \quad (4)$$

$$\text{where } A = 5333.2 \sqrt{\frac{\pi N}{kTM}}$$

$$A = 5333.2 \sqrt{\frac{3.1416 \times 6.06 \times 10^{23}}{1.37 \times 10^{16} \times 300 \times 128}} = 3.21 \times 10^{21}$$

$$T = \frac{1}{\sigma^2 \times 10^{-10} p \times 3.21 \times 10^{21}} = \frac{31.2 \times 10^{-7}}{\sigma^2 p} \text{ sec.} \quad (5)$$

As first approximation we will allow $T = \tau = 10^{-7}$ sec. the mean life of the active state.

$$\text{then } p = 31.2/\sigma^2 \quad (6)$$

where σ is in angstrom units.

The value 2\AA for the diameter of the HI molecule given by W. C. McLewis³⁰ appears to be too small. From considerations above, namely that the hydrogen nucleus is buried within the iodine shell, the diameter of the normal HI molecule should be comparable with that of an I^- ion which, having the stable configuration of Xe should approximate the diameter of the latter. A comparison of the diameters may be made by calculating the diameter of HI from van der Waals' b . Unfortunately only the critical data for HCl and HBr are available, but by plotting b calculated from the critical data in the Landolt-Börnstein tables, against atomic number we arrive at a value $b = 2162 \times 10^{-6}$ for HI, whence $\sigma = 3.37\text{\AA}$. This compares well with 3.42\AA for Xe. In a similar way the values for HBr and Kr are 3.27\AA and 3.14\AA respectively. Since we are concerned with a collision between an excited and a normal molecule of HI some knowledge of the excited state is desirable. Cario³¹ found in the case of Hg, that the diameter increased from 2.8\AA for the normal state to 9.1\AA for the excited state. Assuming in the extreme that the diameter of the excited HI molecule increased to 10\AA and substituting in (6) we obtain as a lower pressure limit

$$p = \frac{31.2}{(5 + 1.69)^2} = 0.693 \text{ m.m. Hg.}$$

In order to be well within the critical pressure it was decided to work with pressures of HI of about 0.1 m.m. Hg. At pressures lower than this it becomes very difficult to measure the absorbed radiation.

Since T is merely the time between collisions it is not strictly true that a collision will never occur within 10^{-7} sec. after absorption of radiation. One has to calculate the probability that a molecule will collide while still in the excited state. A method for this calculation has been worked out by L. A. Turner³² and is applied to the present case.

If τ is the average life of the excited state, then assuming random distribution of lives of excited molecules,

$e^{-t/\tau}$ is the chance that a molecule will remain excited in time t .

If T is the average time between successive collisions of an excited HI molecule and ordinary HI molecules,

$e^{-t/T}$ is the chance that a molecule will not collide in time t
 $e^{-t+dt/T}$ is the chance that a molecule will not collide in time $t + dt$
 The probability that the molecule will collide in the time between t and $t + dt$ is the difference between the last two probabilities. Expanding and keeping only the term with dt to the first power, gives:

$$e^{-t/T} (e^{-dt/T} - 1) = e^{-t/T} dt/T$$

The probability that the molecule will collide in the time between t and $t + dt$ while still in the excited state is the product of the probabilities for collision and duration of the excited state.

$$e^{-t/T} e^{-t/\tau} dt/T = e^{-(T+\tau)t/T\tau} dt/T$$

The probability that a molecule will collide while in the excited state for all values of t is

$$P = \int_0^{\infty} e^{-\frac{(T+\tau)t}{T\tau}} dt/T = -\tau/(T+\tau) \left[e^{-(T+\tau)t/T\tau} \right]_0^{\infty} = \tau/(T+\tau)$$

Thus the probability of a collision while the excited state exists is the ratio of the life of excited state and the sum of the time between collisions and the life of the excited state. We may now determine what percentage of the active molecules collide while still excited. Employing equation (5) and the experimental pressure of 0.1 mm. Hg. of HI,

$$T = \frac{31.2 \times 10^{-7}}{(6.69)^2 \times 0.1} ; T = 6.93 \times 10^{-7} \text{ sec.}$$

$$P = \frac{10^{-7}}{(6.93 + 1) 10^{-7}} = 12.6\%$$

Thus choosing the most unfavorable conditions only 12.6% of the excited molecules collide while still excited while assuming no change in the diameter this reduces to only 3.5%.

Experimental

The method consists in illuminating HI gas at about 0.1 m.m. Hg pressure, measuring the radiation absorbed and the extent of decomposition by freezing out the I_2 and HI and determining the residual H_2 . Only the early stage of decomposition was studied to avoid secondary absorption by the iodine liberated.

a. Apparatus. The experimental arrangement is shown in Fig. 1. L, the source of radiation, consists of a condensed zinc spark, equipped with a micrometer for fine adjustment, connected in parallel with a large plate glass condenser immersed in transformer oil. This in turn was in parallel with the secondary of a large transformer coil whose primary took 65 amps, at 110v. A. C. The latter stepped up to about 40,000v. The electrodes were vertical and were cooled by a blast of nitrogen to prevent oxidation of the Zn and consequent absorption of the ultra-violet bands by the fog of ZnO. In this way a steady spark was maintained.

The optical system O, consisting of a large quartz prism and suitable lenses, served to separate the two strong Zn ultra-violet bands at $\lambda = 2080\text{\AA}$ and $\lambda = 2530\text{\AA}$ ³³ which were also employed by Warburg. The parallel beam was arranged to just illuminate the entire rear window of the quartz cell. By means of an opening in a zinc sulphide fluorescent screen S, on which the lines were sharply and brilliantly defined, either of the bands could be utilized at will.

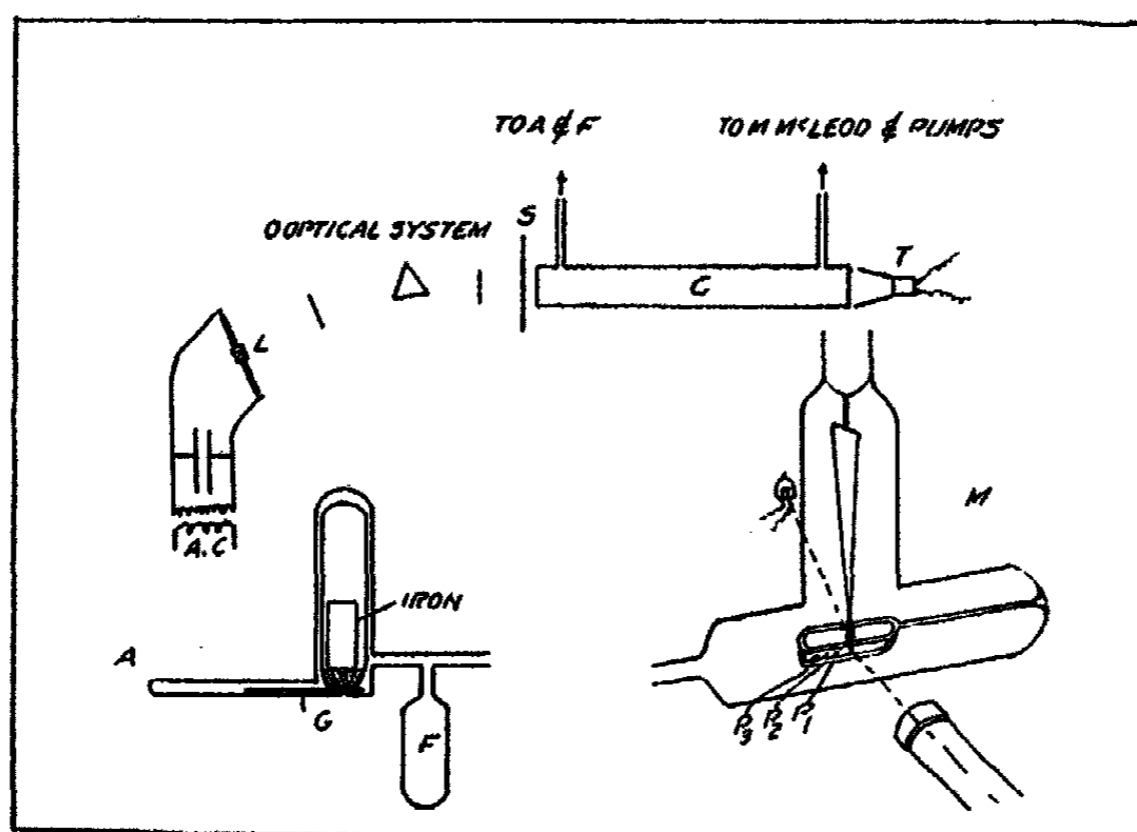


FIG. 1

The clear quartz reaction cell, C, 30.1 cms. long and 2.7 cm. in diameter was provided with optically plane and parallel ends and two quartz-to-pyrex graded joints, connected on the one side to a liquid-air trap, F, and a magnetic hammer device, A, (shown enlarged) for fracturing a small capillary, G, filled with HI, and on the other to a bifilar quartz fibre manometer, M, (shown enlarged) for measuring small pressures of H_2 , a carefully calibrated McLeod gauge and mercury vapor high vacuum pumps. A cadmium-liquid-air trap was used to protect the apparatus, mercury pumps and McLeod. The two quartz fibres in the manometer were sealed together at one end to a small glass indicator³⁴ to prevent elliptical motion as suggested by Coolidge.³⁵ The radiation was measured with a sensitive galvanometer protected from stray magnetic fields, and a Moll thermopile, T, equipped with a fluorite window and receiving funnel 2.60 cms. in diameter.

b. Calibration of Moll Thermopile. The thermopile was calibrated against a standard radiation lamp furnished by the Bureau of Standards. Accompanying directions kindly provided by Dr. Coblenz were rigidly adhered to. The table accompanying the lamp is reproduced in Table I.

TABLE I

| Amps | Volts | Radiation intensity Watt/m.m. ² Distance two meters from lamp |
|-------|-------|--------------------------------------------------------------------------------|
| 0.250 | 79.9 | 42.6×10^{-8} watts |
| 0.300 | 94.8 | 62.7×10^{-8} " |
| 0.350 | 109.8 | 86.7×10^{-8} " |
| 0.400 | 125.0 | 114.4×10^{-8} " |

Table II shows the calibration results, the second column giving the total radiation received by the thermopile (the area of the funnel being 530.7 mm^2). Experiments indicated that all the radiation entering the funnel reached the thermo-couple. The fourth column allows for absorption of a fluorite window indicated in the directions.

TABLE II

| Amps | Total Radiation Watt/sec. | Deflection of Galvo. in m.m. | Flux/m.m. de- flection allowing 91.6% fluorite transmission; watt /sec./m.m. | Average value of Flux; ergs/ sec./m.m. |
|-------|------------------------------|---------------------------------|------------------------------------------------------------------------------------------|-------------------------------------------------|
| 0.250 | 22.61×10^{-6} | 300.0 | 6.91×10^{-7} | |
| 0.300 | 33.27×10^{-6} | 443.1 | 6.88×10^{-7} | 6.87 |
| 0.350 | 46.01×10^{-6} | 618.3 | 6.82×10^{-7} | |

Calculation of number of Quanta received by the thermopile per second per m. m. deflection.

I. For $\lambda = 2080 \text{ \AA}$.

$E = h\nu = hc/\lambda$ where h is Planck's constant
 c is velocity of light in cm/sec.
 λ is wave-length in cm.

$$E = \frac{3 \times 10^{10} \times 6.55 \times 10^{-27}}{2080 \times 10^{-8}} = 9.45 \times 10^{-12} \text{ erg (value of one quantum)}$$

$$\frac{6.87}{9.48 \times 10^{-12}} = 7.27 \times 10^{11} \text{ quanta/sec./m.m.}$$

II. For $\lambda = 2530 \text{ \AA}$.

$$E = \frac{3 \times 10^{10} \times 6.55 \times 10^{-27}}{2530 \times 10^{-8}} = 7.77 \times 10^{-12} \text{ erg.}$$

$$\frac{6.87}{7.77 \times 10^{-12}} = 8.84 \times 10^{11} \text{ quanta/sec./m.m.}$$

c. *Calibration of the Quartz-fibre Manometer.* Since hydrogen was to be measured, the manometer was calibrated at low pressures against the McLeod using pure dry hydrogen, the time of decay of the amplitude of vibration of the indicator between the glass points p_1 and p_2 being noted for different pressures. Care was exercised to exclude all Hg vapor. The image of p_1 and p_2 was observed with a traveling micro-telescope with cross-hair. Care must be taken to preserve the distance between the position of the swinging fibres when at rest and the points p_1 and p_2 . By plotting the pressure of H_2 against the reciprocal of the decay time practically a straight line was obtained at low pressures. All conditions were maintained the same as existed in the actual experiments.

d. *Preparation of capillaries containing HI gas.* The volume of the reaction system which included the quartz cell, manometer, liquid-air trap and magnetic hammer, was 232.5 c.c. A series of small capillaries about 1 m.m. in diameter and 4 to 6 cms. long were constricted at the proper length such that their volumes were approximately 1/7600 of the reaction system. Such a capillary filled with HI at standard conditions would when fractured give a pressure of about 0.1 m.m. HI. The exact pressure could be determined by calibration of the capillary. HI was drawn from a specially prepared strong solution for the use of which I wish to thank Professor S. C. Lind. The HI gas was frozen out in a liquid air trap, water vapour being removed by a $CaCl_2 - P_2O_5$ tube and most of the I_2 by a freezing bath. All of the I_2 was removed by 3 or 4 low temperature distillations. Further purification was effected just before filling the capillaries by 3 low temperature distillations under high vacuum. The capillaries were thoroughly evacuated and HI allowed to expand into them. The pressure was relieved to that of the atmosphere by gently heating the end of a small piece of constricted glass and then quickly sealing. Each capillary was removed in turn at the fine restrictions with a minute jet flame. In this way a very pure HI gas was obtained.

e. *Experimental procedure.* The experimental procedure was as follows: After the reaction system was thoroughly and completely evacuated, the tip of a capillary was broken and the HI frozen out in the liquid air trap. The pumps were again connected to remove the slightest trace of H_2 that may have been present in sealing off the capillary. The amplitude decay time for high vacuum and the galvanometer reading for incident radiation at a given setting of the electrodes were taken before and after each run and were found to check well. The HI was allowed to expand into the reaction system and exposed to the desired ultraviolet band, galvanometer readings being taken every 10 seconds, and after a given time of irradiation it was frozen out together with the I_2 formed. The decay time for the residual H_2 was noted and the pressure read from the calibration chart. From this was calculated the number of molecules of HI decomposed. The energy absorbed was the difference between the galvanometer readings for incident radiation and the average reading while the decomposition was in progress. The various parts

of the apparatus and light source were carefully shielded and the reaction system covered with black paper. The experiments were conducted in a dark room free from draughts, the temperature being about 27°C.

Results

Before presenting the results certain corrections must be made. The absorption of radiation of one quartz plate must be determined. This was found to amount to 15.2% for the line $\lambda = 2080\text{\AA}$ and 8.85% for the line $\lambda = 2530\text{\AA}$. Therefore the total absorption of the lines must be multiplied by the factors 1.18 and 1.097 respectively. A correction for difference in areas between that of the cell window and the thermopile necessitates a further multiplication of the absorption measurements by 1.08 (The area of the window was 573 m.m.² as against 530.7 for the thermopile). Table III presents the results of a series of runs carried out with each line.

A sample calculation from data in experiment 2 will illustrate the method.

| | |
|----------------------------------------------------------------------------------------------------------|-------------------------|
| Absorption in m.m. | 7.83 |
| Time of exposure in seconds | 516 3/5 |
| No. of quanta absorbed/sec./m.m. ($\lambda = 2080$) | 7.27×10^{11} |
| Correction for quartz window absorption | 1.18 |
| " " area of cell | 1.08 |
| Total quanta absorbed = $7.27 \times 10^{11} \times 516 \frac{3}{5} \times 7.83 \times 1.18 \times 1.08$ | $= 3.76 \times 10^{16}$ |
| Pressure of H ₂ in m.m. Hg | 0.0007 |
| Volume of cell | 232.5 c.c. |

Total molecules of HI decomposed =

$$2 \left(\frac{0.0007}{760} \times \frac{273}{300.2} \times \frac{232.5}{22400} \times 6.06 \times 10^{23} \right) = 10.5 \times 10^{16}$$

$$\frac{10.5 \times 10^{16}}{3.76 \times 10^{16}} = 2.79 \text{ molecules/h}\nu$$

The difficulty of measuring the absorption of radiation increases greatly at low pressures. It is therefore desirable to determine whether the measurements are of the correct order of magnitude. This can be done by calculating the coefficient of absorption from the above data using Beer's law and comparing it with the value found by Warburg at higher pressures. The average value for μ , the absorption coefficient, was found to be 0.0427 and 0.0251 for $\lambda = 2080\text{\AA}$ and $\lambda = 2530\text{\AA}$ respectively whereas Warburg found 0.0270 and 0.0139. Warburg's values varied for different set-ups of the apparatus. However the coefficients are of the right order of magnitude and the agreement satisfactory.

TABLE III

| Expt. No. | Primary Current of HI Amps. m.m.Hg. | Pressure of HI m.m.Hg. | Time of exposure seconds | Absorption m.m. de- flection | % Absorp- tion | Total ab- sorption in Quanta (corrected) | Distance between electrodes in revolutions* | Decay time seconds | Pressure Hydrogen m.m. Hg. | Temp. °C. | Total no. molecules decomposed | Molecules decomposed per. hr |
|--------------------------|----------------------------------------|---------------------------|-----------------------------|------------------------------------|----------------------|---------------------------------------------------|---------------------------------------------------------|-----------------------|----------------------------------|--------------|--------------------------------------|------------------------------------|
| $\lambda = 2080\text{A}$ | | | | | | | | | | | | |
| 2 | 65 | — | 516½ | 7.83 | 17.5 | 3.76 × 10 ¹⁵ | 2.5 | 157½ | 0.0007 | 27.2 | 10.5 × 10 ¹⁵ | 2.79 |
| 3 | 66 | — | 1294 | 7.50 | 17.2 | 9.02 × 10 ¹⁵ | 2.5 | 153½ | 0.00162 | 27.1 | 24.3 × 10 ¹⁵ | 2.61 |
| 4 | 67 | 0.144 | 1107½ | 7.10 | 17.5 | 7.30 × 10 ¹⁵ | 2.5 | 156½ | 0.0009 | 26.5 | 13.55 × 10 ¹⁵ | 1.86 |
| 5 | 68 | 0.1585 | 1070 | 6.85 | 15.8 | 6.80 × 10 ¹⁵ | 2.5 | 156½ | 0.0009 | 26.5 | 13.55 × 10 ¹⁵ | 1.99 |
| 6 | 66.5 | 0.104 | 911 | 3.70 | 11.7 | 3.12 × 10 ¹⁵ | 2.25 | 157½ | 0.00074 | 27.0 | 11.1 × 10 ¹⁵ | 3.55 |
| 7 | 68 | 0.117 | 1299½ | 6.95 | 16.5 | 8.37 × 10 ¹⁵ | 2.5 | 157½ | 0.0007 | 27.2 | 10.5 × 10 ¹⁵ | 1.25 |
| $(\text{AV.}) 2.36$ | | | | | | | | | | | | |
| $\lambda = 2530\text{A}$ | | | | | | | | | | | | |
| 8 | 67 | 0.140 | 1206½ | 4.05 | 7.98 | 5.12 × 10 ¹⁵ | 3.5 | 158½ | 0.00054 | 27.3 | 8.10 × 10 ¹⁵ | 1.58 |
| 9 | 68 | 0.156 | 1757½ | 2.7 | 7.94 | 4.98 × 10 ¹⁵ | 2.5 | 150½ | 0.0009 | 27.8 | 13.5 × 10 ¹⁵ | 2.74 |
| 10 | 68 | 0.108 | 1390½ | 2.9 | 9.2 | 4.23 × 10 ¹⁵ | 2.5 | 157.9 | 0.00064 | 27.5 | 9.6 × 10 ¹⁵ | 2.27 |
| 11 | 69 | 0.108 | 1113½ | 3.3 | 11.0 | 3.86 × 10 ¹⁵ | 2.5 | 157½ | 0.00072 | 27.4 | 10.8 × 10 ¹⁵ | 2.79 |
| $(\text{AV.}) 2.35$ | | | | | | | | | | | | |

*One revolution corresponds to a distance of 1/16 inch.

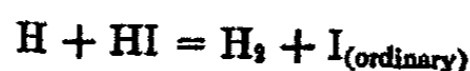
Discussion of Results

It is observed that the number of molecules decomposed for each quantum absorbed is about two as Warburg also found at higher pressures (80 m.m. to 350 m.m.). This indicates that an activated hydrogen-iodide molecule does not require a collision to suit its condition for decomposition.

A question of interest is the fate of the surplus energy namely the difference between the absorbed 137,000 calories ($\lambda = 2080\text{\AA}$) and 68,000 calories the heat of decomposition of HI from thermochemical data, or 69,000 calories. The first electron level for the hydrogen atom is 10.2 volts or 236,000 calories. Thus excitation of the hydrogen atom is out of the question. From theoretical considerations and spectroscopic data Franck and Kuhn²⁵ have pointed out that HI like AgI is a non-ion linkage, the first stage in its dissociation as shown by the long wave-length limit of its continuous absorption spectrum, taking place not into two normal atoms but into a normal and excited atom. No maxima were observed in the continuum down to $\lambda = 2000\text{\AA}$ and thus no transition occurs in the mode of decomposition and therefore in the type of binding. From the long wave-length limit of the continuous absorption band, about $\lambda = 3200\text{\AA}$, we obtain 89,000 calories. This value, less the heat of dissociation of HI gives 21,000 calories which is just the energy required to excite the iodine atom from the stable $2P_2$ state to the metastable $2P_1$ state. It is noteworthy that absorption does not begin at a point where the energy is just equal to the heat of dissociation of HI; therefore the latter cannot dissociate into two normal atoms. Similarly in the case of I_2 the energy corresponding to the band convergence limit where the molecule begins to dissociate, exceeds the dissociation energy by about 0.9v. or 21,000 calories, which represents dissociation into a normal and an excited atom in the $2P_1$ state. There remains 48,000 calories to be accounted for. An attempt was made to observe a visible fluorescence in the iodine liberated but without success. That the iodine atom is not excited further than that represented by the $2P_1$ state is evident from the present results for otherwise a quantum efficiency of 4 would be expected particularly at low pressures where complicating secondary effects prevalent at higher pressures, are absent. By a collision of the second kind the endothermic reaction (about -28,000 calories)



could proceed and then



The quantum efficiency at low pressures being slightly in excess of 2 may be explained on the basis of the occasional occurrence of the above process with an iodine atom in the $2P_1$ state possessing an exceptional velocity dictated by Maxwellian distribution. It must be concluded that the 48,000 calories are dissipated as kinetic energy.²⁶ In the division of this energy between the hydrogen and iodine atoms, nearly all of it is assumed by the hydrogen on the principle of conservation of momentum. This accounts for the fact that

every impact between H and HI (a reaction which is ordinarily exothermic but which nevertheless possesses a critical energy increment for reaction by collision) results in the decomposition of the latter.

It is of interest to note that since collisions are unnecessary for the dissociation of HI, the time between absorption of radiation and decomposition may be less than 2×10^{-10} sec., the average time between collisions as calculated from Warburg's highest pressure.

From the spectroscopic side it may be concluded that the same interpretation of the continuous spectrum exhibited by hydrogen-iodide may be adopted as was proposed for non-polar molecules; that gaseous hydrogen-iodide dissociates in a single and elementary act after absorption of radiation into a normal hydrogen atom and an excited iodine atom.

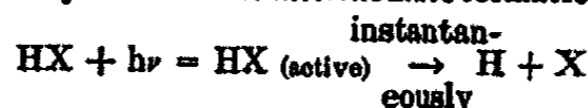
Summary

The photochemical dissociation of hydrogen-iodide was studied at low gas pressure where the collision frequency is comparable with the mean life of the excited state. Quantum efficiency of the process was found to be about 2 which agrees with Warburg's value for high gas pressures. This indicates that hydrogen-iodide dissociates in an elementary act as a result of absorption of radiation without the necessity of a collision. From the continuous absorption spectrum it is shown that dissociation takes place into a normal hydrogen atom and an excited iodine atom in the metastable $2P_1$ state, the excess energy if any, being dissipated as kinetic energy. It is pointed out that the time between absorption and dissociation is shorter than 2×10^{-10} sec.

It is a pleasure to acknowledge the kind interest shown by Professor S. C. Lind during the progress of this work.

References

- ¹ Preliminary notices in *Nature*, 119, 493 (1927) and *Proc. Nat. Acad. Sci.*, 13, 720 (1927).
- ² National Research Fellow in Chemistry.
- ³ *Sitz. Akad. Wiss. Berlin*, 1916, 314; 1918, 300.
- ⁴ This mechanism virtually includes the intermediate formation of an active HI molecule.



H. Kuhn (*Z. Physik*, 39, 77 (1926)) concludes from an analysis of the band and continuous absorption spectrum of the halogens that excitation of the molecule does not enter into the question but rather an immediate dissociation into a normal and excited atom occurs in an elementary act without a collision.

⁵ *Z. wiss. Phot.*, 19, 275 (1920).

⁶ Henglein: *Z. anorg. Chem.*, 123, 137 (1922).

⁷ Kuhn: *Z. Physik*, 39, 77 (1926).

⁸ P. Pringheim: "Fluorescenz und Phosphorescenz" (1923).

⁹ For literature see Franck: *Physik. Z.*, (1918), or Foote and Mohler: "Origin of Spectra."

¹⁰ O. Oldenberg: *Z. Physik*, 18, 1 (1923).

¹¹ J. Franck: *Trans. Faraday Soc.*, 21, 536 (1926).

¹² $[\text{HX}]_2 + \text{HX} = \text{H} + \text{X} + \text{HX}$ etc. Another mechanism suggests itself namely the clustering of molecules. However, absorption by a double molecule to bring about decomposition into a halogen molecule and a hydrogen molecule cannot exist since temperature or pressure has no effect on the absorption. (Coehn and Stuckardt: *Z. physik. Chem.*, 91, 722 (1916); Warburg: *lc.*; and Tingey and Gerke: *J. Am. Chem. Soc.* 48, 1838 (1926)).

¹³ R. C. Tolman: *Phys. Rev.*, 23, 693 (1924).

¹⁴ M. Bodenstein: *Trans. Faraday Soc.*, 21, 525 (1926).

¹⁵ M. Bodenstein: *Z. physik. Chem.*, 22, 23 (1897).

¹⁶ *Z. wiss. Phot.*, 24, 177 (1926).

- ¹⁷ Since we are dealing with an activation consisting primarily of a change in electronic quantum state, the life of the active state for emission is of the same general order of magnitude as the mean life of other systems involving roughly similar electron jumps, namely about 10^{-7} sec. (For literature see Franck and Jordan: "Anregung von Quantumsprüngen durch Stöße," (1926).
- ¹⁸ Tingey and Gerke: *J. Am. Chem. Soc.*, 48, 1838 (1926).
- ¹⁹ Franck, Kuhn and Rollefson: *Z. Physik*, 43, 155 (1927); Birge and Sponer: *Phys. Rev.*, 28, 259 (1926); Leifson: *Astrophys. J.*, 63, 73 (1926); E. E. Witmer: *Proc. Nat. Acad. Sci.*, 12, 238 (1926).
- ²⁰ F. Hund: *Z. Physik*, 40, 742 (1927).
- ²¹ V. Kondratjew: *Z. Physik*, 39, 191 (1926).
- ²² The possibility of a dissociation into these component parts is borne out by the appearance of a third maximum in the continuous absorption of NaI (Franck, Kuhn and Rollefson: loc. cit).
- ²³ Both the absorption of radiation and the number of collisions are proportional to the pressure.
- ²⁴ A. Terenin: *Z. Physik*, 37, 98 (1926).
- ²⁵ Franck and Kuhn: *Z. Physik*, 43, 164 (1927).
- ²⁶ Bell: *Phil. Mag.*, 47, 549 (1924).
- ²⁷ It may be significant that the electron affinity of I^- calculated from Born's method of grating energy of crystals as 81,000 calories (Foote and Mohler: "Origin of Spectra") is quite close to that evaluated from the long wave-length limit of the continuous absorption of HI. It is therefore possible that HI will only dissociate when sufficient energy has been absorbed to cause I^- to part with its extra electron. In the final adjustment, the energy over and above the thermochemical value goes to excite the iodine atom as will appear later.
- ²⁸ F. Simon and C. Simon: *Z. Physik*, 21, 168 (1924).
- ²⁹ The concentration of active HI molecules at any time is negligibly small compared with the total concentration. Therefore impacts between active molecules may be neglected.
- ³⁰ *J. Chem. Soc.*, 113, 473 (1918).
- ³¹ *Z. Physik*, 10, 188 (1922).
- ³² *Phys. Rev.*, 23, 464 (1924). I am indebted to Dr. George Glockler for bringing this work to my notice.
- ³³ Weighted mean—Eder: *Z. wiss. Phot.*, 13, 38 (1913); Pffüger: *Ann. Physik*, 13, 904 (1904).
- ³⁴ The fibres are easily joined to glass by inserting them in a capillary opening in the glass indicator and heating the latter locally until the walls just touch.
- ³⁵ *J. Am. Chem. Soc.*, 45, 1637 (1923).
- ³⁶ This conclusion is in agreement with the theory of Franck. A private communication from T. R. Hogness working in Göttingen, Germany, states that when gaseous NaI molecules are excited by a frequency greater than that necessary for dissociation, the excess energy is dissipated in the form of kinetic energy of the dissociating atoms. The greater the excess energy the greater the kinetic energy of the dissociating atoms, hence the greater the Doppler effect of the D lines emitted.

School of Chemistry,
University of Minnesota,
September 1, 1927.

THE VOLUME CHANGES ATTENDANT ON MIXING PAIRS OF LIQUIDS

BY JOHN BUTTERY PEEL, WALTER MATTHEW MADGIN, AND
HENRY VINCENT AIRD BRISCOE

It has been held¹ that the changes in volume and temperature occurring when liquids are mixed are closely related. It has been shown, however, (1) that a decrease in volume may accompany a fall in temperature, and that even when a decrease in volume is associated with a fall in temperature the maxima of these effects may occur with mixtures of different compositions² and (2) the diminution in volume in a given case (chloroform: ether) was much less than the heat of mixing³ would suggest. From a consideration of several cases, Young⁴ concluded that "the thermal and volume effects do not, in many cases, run *pari passu*, though where a rise of temperature accompanies an increase in volume, or vice versa, both effects are relatively small."

Though two investigations⁵ have dealt with the relationship between changes in volume and in other physical properties, none has yet dealt systematically with the possible connection between volume change and thermal effect in binary mixtures. It was, indeed, a prior condition of such an investigation that a broad survey should be made of the sign and magnitude of the thermal effects in a large number of cases, and this has but recently been done.⁶

It has now been possible to select a number of pairs of liquids covering a wide range of thermal effects, and for these to determine in a systematic fashion the variation of change of volume on mixing. The results of this work are given here.

Experimental

The volume changes for each liquid pair were found by determining the densities of the pure liquids and several mixtures of known composition, using 30 cc. silica Sprengel pyknometers having a bulb on the short limb and ground silica caps on both limbs to prevent evaporation. Irregular results obtained at first with both glass and silica pyknometers were traced to changes in the composition of liquid mixtures by fractional evaporation during filling by suction. Possibly such evaporation effects account for the very irregular results previously obtained for some liquid pairs (e.g., Bussy and Buignet for ethyl alcohol: carbon disulphide). Therefore, in the determinations recorded, the pyknometer was filled by forcing the liquid into it from a closed vessel in a

¹ See E. G. Guthrie: *Phil. Mag.*, (5) 18, 495 (1884); Patterson and Montgomerie: *J. Chem. Soc.*, 95, 1136 (1909).

² Bussy and Buignet: *Ann. Chim. Phys.*, (4) 4, 5 (1865).

³ Clarke: *Physik. Z.*, 6, 154 (1905).

⁴ "Distillation Principles and Processes" (1922).

⁵ Brown: *J. Chem. Soc.*, 39, 202 (1881); Bramley: 109, 434 (1916).

⁶ Briscoe and Madgin: *J. Soc. Chem. Ind.*, 46, 107 (1927).

manner similar to that described by Briscoe, Robinson and Stephenson, the vessel B being replaced by a large test-tube fitted with a rubber stopper carrying the tubes P and H. A mercury-filled Hempel burette was used to apply air-pressure through H.

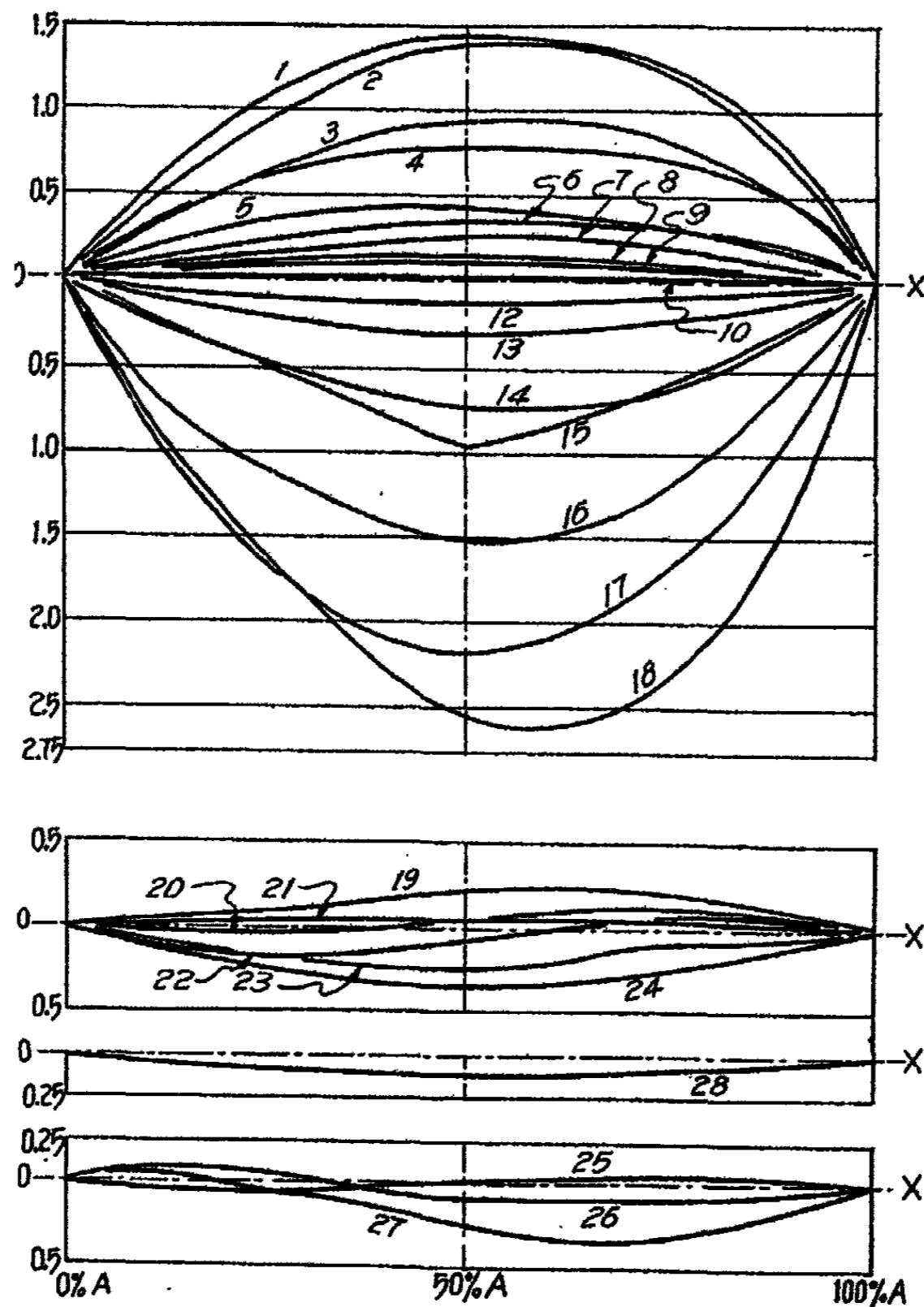


FIG. 1

In preparing the liquid mixtures (approximately 50 cc. for each experiment) the proper quantity of the more volatile liquid was weighed into a well-stoppered concial flask, and a measured volume of the second liquid was run in while the flask was kept cooled in running water. Thereafter the flask

¹ J. Chem. Soc., 129, 731 (1926) Fig. 3.

was immediately closed, and reweighed, the weighings being made against a tare and with all usual precautions. From the weight-composition of the mixture thus determined, the volume-composition was calculated, using the ascertained densities of the pure liquids.

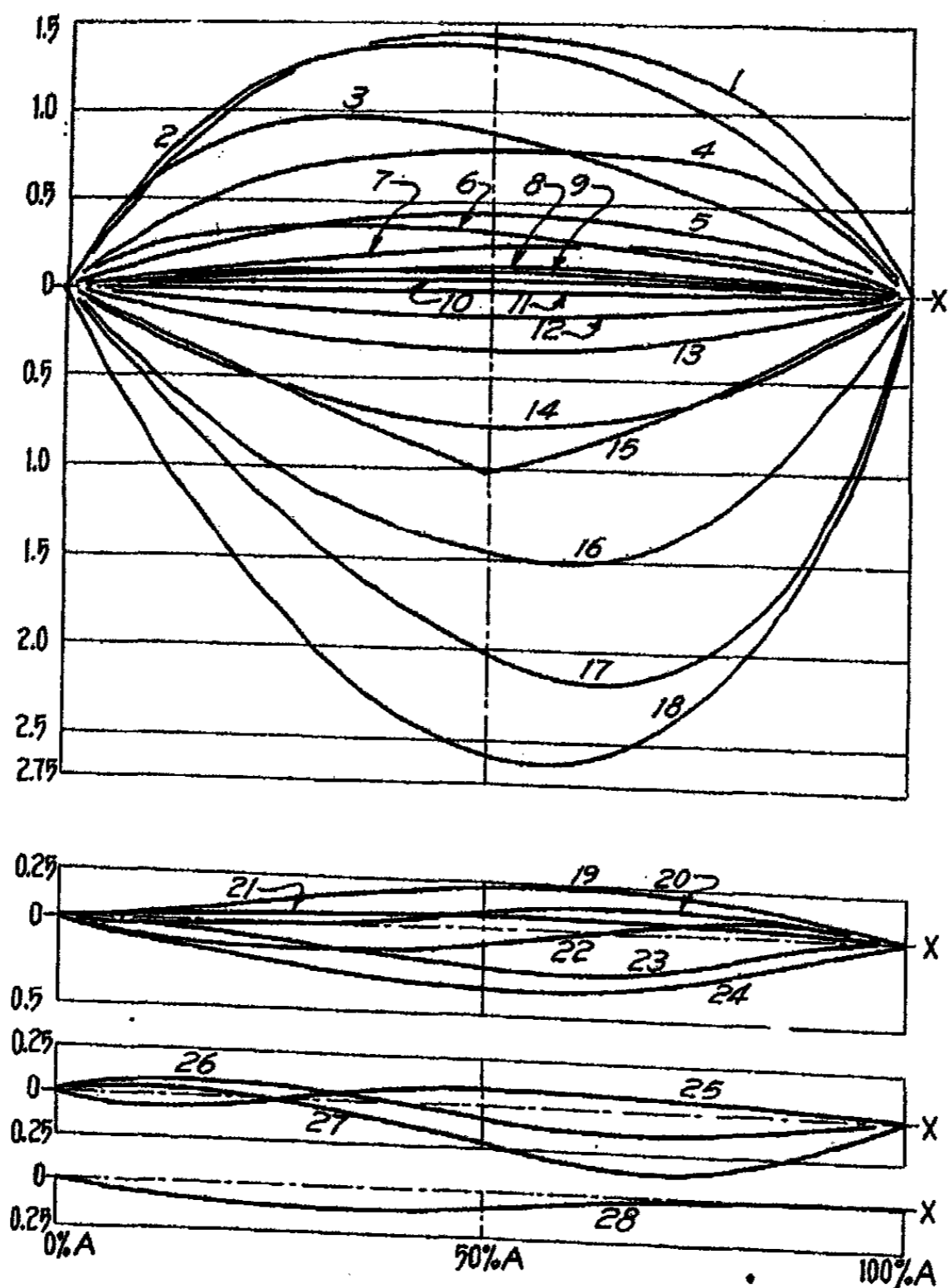


FIG. 2

The pycnometer, after filling, was brought exactly to $25^{\circ} \pm .01$ in a thermostat, the level of the liquid was adjusted in the usual way, the caps were fitted, and then the pycnometer was transferred to the balance case and weighed accurately against its tare. *Results.* The results are shown graphically in Figs. 1 and 2, where the volume changes, (positive above and negative below the OX axis) in cc. per 100 cc. of total constituent liquids, derived in an obvious way from the experimental data, are plotted as ordinates against the mixture-compositions as abscissae. The figures differ in that the composition

is expressed in Fig. 1 as volume percentage and in Fig. 2 as gram-molecular percentage. It is noticeable, and may be significant, that the curves in Fig. 1 tend to be more symmetrical than those in Fig. 2.

TABLE I

| I No. | II Pairs of liquids mixed (A + B) | | III | IV Volume change. Per cent for mixing 10 cc A 50% (volume) + 10 cc B* mixture* | V Temperature change on + 10 cc B* |
|----------|-----------------------------------------|------------------------|-----|-----------------------------------------------------------------------------------------------|---------------------------------------------|
| | A | B | | | |
| 1 | Acetone | : carbon disulphide | E | +1.4 | -9.75 |
| 2 | Ethyl acetate | : carbon disulphide | | +1.35 | -7.25 |
| 3 | Hexane | : acetone | | +0.9 | -7.15 |
| 7 | Ethyl alcohol | : methyl acetate | B | +0.25 | -7.05 |
| 11 | Ethyl alcohol | : ethyl oxalate | | 0 | -6.85 |
| 25 | Hexane | : ethylene dibromide | | 0 | -6.7 |
| 24 | Aniline | : carbon tetrachloride | | -0.3 | -5.85 |
| 8 | Ethyl alcohol | : ethyl acetate | C | +0.10 | -5.3 |
| 4 | Ethyl alcohol | : carbon disulphide | A | +0.75 | -5.2 |
| 5 | Aniline | : o-dichlorobenzene | | +0.4 | -5.05 |
| 6 | Hexane | : carbon disulphide | | +0.3 | -3.35 |
| 12 | Methyl iodide | : ethylene dibromide | | -0.15 | -1.1 |
| 26 | Ethyl alcohol | : carbon tetrachloride | | -0.1 | -0.4 |
| 9 | Benzene | : toluene | D | +0.1 | -0.35 |
| 21 | Ethyl acetate | : methyl acetate | | +0.025 | -0.05 |
| 13 | Chloroform | : ethylene dibromide | G | -0.3 | +0.35 |
| 10 | Chloroform | : methyl iodide | | +0.025 | +1.45 |
| 14 | Ether | : carbon tetrachloride | | -0.75 | +2.75 |
| 18 | Ether | : aniline | K | -2.55 | +3.1 |
| 27 | Ethyl alcohol | : chloroform | F | -0.25 | +3.95 |
| 23 | Methyl alcohol | : chloroform | | -0.225 | +5.5 |
| 16 | Acetone | : aniline | B | -1.5 | +6.3 |
| 19 | Methyl acetate | : chloroform | | +0.2 | +8.45 |
| 20 | Ethyl acetate | : chloroform | | +0.05 | +9.8 |
| 28 | iso-Amyl acetate | : chloroform | | -0.1 | +10.5 |
| 22 | Acetone | : chloroform | E,H | -0.1 | +12.65 |
| 15 | o-chloro phenol | : aniline | J | -1.0 | +13.85 |
| 17 | Ethyl alcohol | : o-chlorophenol | | -2.2 | +14.25 |

References in III.

A—Bussy and Buignet: *Ann. Chim. Phys.*, (4), 4, 5 (1865).B—Matthews and Cooke: *J. Phys. Chem.*, 18, 566 (1914).C—Merriman: *J. Chem. Soc.*, 103, 1787 (1913).D—Young and Fortey: *J. Chem. Soc.*, 83, 45 (1903).

E—Young: "Distillation Principles and Processes," 34 (1922).

F—Brown: *J. Chem. Soc.*, 39, 202 (1881).G—Dobroserdoff: *J. Russ. Phys. Chem. Soc.*, 44, 679 (1912).H—Holmes: *J. Chem. Soc.*, 103, 2163 (1913).J—Bramley: *J. Chem. Soc.*, 109, 434 (1916).K—Hartung: *Trans. Faraday Soc.*, 21, 66 (1917).

*In columns IV and V of the table, the positive sign (+) indicates an increase in volume or rise in temperature, and the negative sign (-) the reverse.

Table I affords a key to Figs. 1 and 2, giving the numbers (Col. I), corresponding with the 28 pairs of liquids (Col. II), being used to indicate their volume-curves in the Figures; the Table also shows for each liquid-pair the percentage volume-change (Col. IV) and the temperature change at 20° (Col. V) for the 50 per cent volume mixture. Certain prior results in isolated cases are indicated by the references in Col. III. Sometimes the earlier results differ from those now reported. Brown in the case of ethyl alcohol: chloroform reported a contraction for all compositions, but his curve, being based on three determinations only, happened not to show the small expansion which occurs with high proportions of chloroform. Holmes (loc. cit. p. 2162) concludes that methyl iodide and chloroform give "a small but appreciable expansion" on mixing and this is in agreement with curve 10 now reported. Aniline: carbon tetrachloride (24) give a contraction with a fall in temperature on mixing and Hartung¹ has found that these two liquids react slowly to form a compound. Curve 15 consists of two almost straight lines and this is in agreement with what Bramley² has found for the same mixture.

A careful scrutiny of Columns IV and V brings out with great clarity the chief result of this investigation: the volume and temperature changes evidently bear no relation to each other. A glance at cases 22 and 18 shows at once that there is no tendency even to a constancy of ratio between volume change and thermal effect.

This conclusion is supported by another consideration. In Table II are given for 20 cc. of 50% vol. mixture of selected liquid pairs, the heat of mixing (Col. IV) and the external work (also in calories) attributable to the observed volume change (Col. VI): these are derived in a manner which is evident from the columns of the Table. Here again it is evident that, in every case, the external work done by or on the mixture, accounts for but an insignificant fraction of the energy change involved. It is true that the method used in calculating Column IV (following precisely that of Kremann³, is likely to give a result in some cases in error by several tens per cent, but this is not of much moment when the difference between Columns IV and VI is many hundreds per cent.

Thus the results here presented afford evidence that practically the whole of the observed thermal effect of mixing liquids must be attributed to *internal* work done thereby. It is commonly believed that relatively great internal pressures exist in liquids and vary widely from one liquid to another: and it is conceivable that the observed thermal effect may be strictly equivalent to the work done in the volume change with or against these pressures. This view could be verified experimentally by determining the compressibility of mixtures formed with increase of volume, but the existence of cases such as Nos. 10, 12, 19, 20, 24, 26, where an increase in volume accompanies a rise of

¹ J. Chem. Soc., 113, 163 (1918).

² J. Chem. Soc., 109, 444 (1916).

³ "Die Eigenschaften der binären Flüssigkeitgemische," 65 (1916).

TABLE II

| I Liquids mixed (10 cc of each liquid) | II Specific heats | | III Temp. change on mixing | IV Weight of mixture in grams | V Heat of mixing in calories | VI Volume change on mixing | VII External work, against atmosphere (760mm.), on mixing Calories |
|-------------------------------------------------|----------------------|-------|----------------------------------------|----------------------------------------------|---------------------------------------------|----------------------------------------|-----------------------------------------------------------------------------------------|
| | A | B | | | | | |
| 22 Acetone : chloroform | 0.52 | 0.23 | +12.65 | 23.2 | +96.8 | -.02 | +.00048 |
| 16 Acetone : aniline | 0.52 | 0.52 | + 6.3 | 18.1 | +59.3 | -0.3 | +.0072 |
| 18 Ether : aniline | 0.535 | 0.52 | + 3.1 | 17.38 | +28.4 | -0.51 | +.0122 |
| 10 Methyl iodide : chloroform | 0.178 | 0.23 | +1.45 | 38.1 | +11.0 | +.005 | -.00012 |
| 12 Methyl iodide : ethylene dibromide | 0.178 | 0.175 | -1.1 | 44.75 | - 8.7 | - .03 | +.00007 |
| 2 Ethyl acetate : carbon disulphide | 0.484 | 0.237 | -7.25 | 21.9 | -54.0 | +0.27 | -.0065 |
| 1 Acetone : carbon disulphide | 0.52 | 0.237 | -9.75 | 20.8 | -70.2 | +0.3 | -.0072 |

temperature on mixing, and vice versa, renders it almost certain that this hypothesis is inadequate, and that a substantial part of the thermal effect, at least in many cases, is due to chemical changes on admixture.

In brief, the study of volume changes leads, as does that of temperature changes, to the conclusion that the observed effects are not properties of liquids in general but specific properties of chemical reagents. This idea is supported by a consideration of cases 19, 20 and 28, where it is evident that both thermal and volume changes vary regularly with progression up an homologous series.

It is perhaps significant, in this connection, that while gases at low concentrations are amenable to the gas laws, they exhibit in high concentrations highly specific deviations from these general laws. At the much higher concentrations existing in liquids, it would appear that the specific properties of the molecules are of primary importance.

This view receives some support from a study of the curves. It is evident that a number of these, e.g. Nos. 19, 20, 22, 23, 25, 26, 27, 28, are sinuous. Such sinuous curves have been obtained by several workers for several properties of liquid mixtures, (see, e.g., viscosity of phenol-pyridine mixtures,¹ vapour pressure of pyridine and water,² density of n-amyl alcohol and acetone, admixed with chloroform³), and Bramley has advanced the explanation that they are due to chemical changes in the liquids concerned.

As a further check, the thermal effects of adding to the 50% volume mixture further quantities of each of the constituent liquids have been examined: the results are given in Table III, as the temperature change in degrees produced on making the mixtures indicated at the top of the column.

TABLE III

| Constituent Liquids | | Temperature Change on Mixing: | | |
|---------------------|---------------------------|-------------------------------|-------------------|-------------------|
| A | B | 5A + 5B | (5A + 5B) + 5A | (5A + 5B) + 5B |
| Ethyl alcohol | : chloroform | +3.7 | +2.6 | -1.3 |
| —do— | : carbon tetrachloride | -0.4 | +0.7 | -0.8 |
| Ether | : chloroform | +1.4 | +3.3 | +2.1 |
| —do— | : carbon tetrachloride | +2.8 | +0.7 | +0.6 |

In the first two cases, where the density composition curves are sinuous, the thermal effects of adding the constituent liquids to the mixtures are opposite in sign: in the last two cases these effects are similar. Thus it seems at least probable that, with an alcohol-chloroform mixture, addition of alcohol

¹ Bramley: J. Chem. Soc., 109, 39, 43 (1916).

² Brønsted: Z. physik. Chem., 68, 693 (1910).

³ Holmes: J. Chem. Soc., 103, 2163 (1913).

favours formation of the alcohol-chloroform complex, addition of chloroform leads to dissociation either of the complex or of the associated molecules of one of the constituents, presumably alcohol.

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October 14, 1937.*

A CONCEPTION OF POLARITY DERIVED FROM PHYSICAL MEASUREMENTS AND ITS RELATIONS TO THE ELECTRONIC CONFIGURATION OF AROMATIC ORGANIC COMPOUNDS

BY J. F. T. BERLINER

Introduction and Discussion

In a recent series of studies on the vapor pressures of a number of highly purified organic compounds several relations were observed that appear to merit further consideration. The compounds studied were the isomeric nitroanilines, mononitrotoluenes, toluidines and naphthols. In this discussion the latter group will be omitted.

Many determinations, direct and indirect, have been made of the heats of vaporization and to the present time but two generalizations have been evolved that can be related to chemical phenomena. The first is, that in general the latent heat per gram is less for substances of higher molecular weight, and the second that a relation exists between the entropy and the latent heat of vaporization that involves a consideration of the association of molecules.

As the kinetic energy associated with each molecule at the same temperature is the same, it follows that, as there are less molecules in one gram of substance of high molecular weight, there is also less total kinetic energy. The latent heat is, therefore, also less. The latent heats of vaporization are not simply inversely proportional to the molecular weight; several factors are involved, the principal ones being the mean square velocity of the molecules escaping from the surface of the liquid and the amount of heat necessary to overcome the intramolecular attraction. The velocity may be calculated from a consideration of the assumption that the ratio of the density of the vapor to the density of the liquid is the ratio of the molecules with sufficient speed to escape from the surface of the liquid to the number with insufficient speed. This assumption is justified in that many physical facts may be explained through it and it does not seem to be opposed to any of our present conceptions of vaporization, or its colligative properties. This idea is also applicable to solutions: Thus the lowering of the vapor pressure of a solvent, by the introduction of a non-volatile solute, is explained by considering that the number of molecules with sufficient speed to escape is thereby reduced relatively to the number with insufficient speed. On account of their electrical

¹ Berliner and May: Studies in Vapor Pressure. I. The Nitroanilines, *J. Am. Chem. Soc.*, **47**, 2350 (1925).

² Berliner and May: Studies in Vapor Pressure. II. The Mononitrotoluenes, *J. Am. Chem. Soc.*, **48**, 2630 (1926).

³ Berliner and May: Studies in Vapor Pressure. III. The Toluidines, *J. Am. Chem. Soc.*, **49**, 1007 (1927).

⁴ May and Berliner and Lynch: Studies in Vapor Pressure. IV. The Naphthols, *J. Am. Chem. Soc.*, **49**, 1012 (1927).

nature, ions have to overcome a greater cohesive force in order to escape and consequently need a much greater kinetic energy than molecules. They are, therefore, largely non-volatile. In a similar way the forces of attraction between water molecules and other non-volatile molecules is probably greater than that between the water molecules themselves.

Recently MacLeod⁶ has published a comprehensive treatise on this phase of the subject and has pointed to a possible analogy between the mechanism of evaporation based on differential surface velocities of molecules and osmotic pressure phenomena. (See p. 542).

The nitroanilines and the nitrotoluenes have however almost the identical molecular weights, 138.06 and 137.06, respectively. From this consideration the same heat of vaporization for each compound might be expected. However, it was observed^{1,2} that the heats of vaporization of the isomers of the nitroanilines differ widely, and those of the nitrotoluenes, besides being very much lower than the heats of vaporization of the nitroanilines, also differ from each other to a small extent. As was indicated in the papers referred to above the nitroanilines appear to form highly associated molecules, while the nitrotoluenes are practically non-polar substances. When the heat of vaporization of an associated substance is arrived at through vapor pressure determinations, a factor is involved that may be called the heat of "deassociation," that is, the amount of heat energy necessary to decompose an associated molecule into normal non-associated molecules. This heat may be quite high and in the case of para nitroaniline is about 6600 calories (value arrived at from consideration of observed and calculated theoretical heat of vaporization) per mole. Therefore the abnormally high heats of vaporization of the nitroanilines may be readily explained and it is evident that one of the fundamental properties that must be taken into cognizance, in arriving at any conclusions from the experimental and derived data, is that of polarity or association. The heats of vaporization, while in themselves important, are dependent on the degree of molecular association and can not be correctly interpreted unless the extent of the latter condition is known.

The relations between the entropy of a liquid and its latent heat of vaporization were soon recognized; though at first the function now denoted as entropy was not recognized. In 1884 Trouton⁶ announced the rule that is now known by his name—that the quotient from the heat of vaporization per mole divided by the absolute boiling point, is approximately the same for all substances. This law has, in fact, been until fairly recently assumed to be at least approximately correct. The value of the quotient is about 20 to 22. The rule as it would now be stated is, that the entropy increase per mole is the same for liquids at their boiling point. It may be said that the validity of this rule would follow from the work of Guldberg⁷ who pointed out that the boiling point on the absolute scale is nearly always about two thirds the abso-

⁶ MacLeod: *Trans. Faraday Soc.*, 20, 525-543 (1925).

⁶ Trouton: *Phil. Mag.*, (5) 18, 54 (1884).

⁷Guldberg, *Z. physik. Chem.*, 5, 374 (1890).

lute critical temperature. A more rigid examination of Trouton's rule, shows, however, that the ratio is by no means constant, but increases regularly with the temperature, as was pointed out by Nernst⁸ and also by Bingham.⁹ Trouton's rule holds very well for non-polar liquids boiling in the neighborhood of 100° to 300°C. It has been derived theoretically from the theorem of corresponding states by Iterson;¹⁰ however, according to Bingham, it must hold more closely than this theorem.

For polar or associated liquids, such as water or alcohol, the Trouton ratio is larger. This is explained, as was previously indicated, by assuming that when a liquid is associated, and its vapor not associated, a certain amount of heat is required to dissociate the molecules of the liquid, hence the normal heat of vaporization is increased. The effect on the boiling point is doubtless not very large, so that when abnormally high values of the ratio are obtained the evidence of dissociation seems very satisfactory. The quotient from the heat of vaporization divided by the absolute boiling point represents the increase in entropy of the substance during vaporization. A rule essentially the same as Trouton's has been given by LeChatelier and Forcrand¹¹ wherein the entropy constant of certain solid compounds at a pressure of one atmosphere is approximately 33 calories per degree. Various modifications have been suggested for Trouton's rule. Two of these have been proposed by Nernst.¹² It is difficult to determine from what Nernst says, whether they have any other than an empirical foundation. They seem chiefly intended to take into account the low-boiling gases. Another formula has been proposed by Bingham¹³ which is also empirical and has been constructed without much reference to liquid boiling at very high or very low temperatures. More recently Forcrand¹⁴ has published a formula, also empirical, but which has attempted to include liquids with very high, as well as those with very low boiling points. The course of this equation at high temperatures was determined by using data for the boiling points of silver and copper. However, Forcrand's formula is not considered very significant.

The most important generalization has been given by Hildebrand,¹⁵ derived from the Clapeyron-Clausius equation of state. The Clapeyron-Clausius equation may be put in the form

$$\frac{d \log p}{d \log T} = \frac{L}{RT}$$

Now L/T is the entropy, so that if $\log p$ be plotted against $\log T$, the tangent to the curve at any point is equal to the entropy divided by R , the gas constant. By plotting a number of curves, it was found that the points, where

⁸Nernst: *Gött. Nachr.* Heft 1, 1906.

⁹Bingham: *J. Am. Chem. Soc.*, 28, 717 (1906).

¹⁰Iterson: *Z. physik. Chem.*, 53, 633 (1905).

¹¹Le Chatelier and Forcrand: *Ann. Chim. Phys.*, 28, 384, 531 (1903).

¹²Nernst: *loc. cit.* See also "Theoretical Chemistry," p. 274 (1911).

¹³Bingham: *loc. cit.* Also see, Sonaglia: *Nuovo Cimento*, 7, 321 (1914).

¹⁴Forcrand: *Compt. rend.*, 156, 1439, 1648, 1809 (1913).

¹⁵Hildebrand: *J. Am. Chem. Soc.*, 37, 970 (1915); 40, 45 (1918).

their tangents had the same slope, were on a straight line which could be represented by $\log p = \log T - \text{constant}$. If the vapor obeys the gas laws then $p = cRT$ where c denotes the concentration. This may be converted into the logarithmic equation, $p = \log T - \log Rc$; therefore $\log Rc$ is the constant of the above equation. Along such a line as represented by this equation, the concentration must be constant, Hildebrand therefore states that: "The entropy of vaporization for normal liquids is the same when evaporated to the same concentration, i.e., when the final mean distance between the molecules of vapor is the same." It must be emphasized that Trouton's rule makes a comparison at constant pressure (one atmosphere) and not at constant concentration, and under constant pressure conditions the entropies are not the same. Any concentration may be chosen. Hildebrand arbitrarily chose the concentration of 0.00507 moles of vapor per liter, this concentration having the "desirability of avoiding any extrapolation" of his measured data. The value for the constant is approximately 13.7 calories per degree.

Applying Trouton's Rule, the increase of entropy constant varies greatly with substances of widely different boiling points; as, for instance, nitrogen and bromonaphthalene give values of 11.0 and 14.1 calories per degree, respectively, while with Hildebrand's expression the values for these two substances are the same—13.8 calories per degree. Hildebrand found that associated substances gave abnormal values, for instance, ammonia, water and ethyl alcohol gave 16.2, 16.0 and 16.7 calories per degree, respectively. He also found a small though significant difference for the metals which were on the average about 0.6 calories per degree lower than the normal liquids. It is suggested that this deviation is due to a difference in molecular complexity. When a molecule escapes from the liquid to the vapor it is relieved of a very high internal pressure which exists in the liquid, and may, conceivably, expand with an absorption of energy. The amount of energy so absorbed would be expected to be greater in the case of molecules containing many atoms than with those containing but a few.

The expression for the entropy of vaporization may therefore be written $(L - e)/RT$, where "e" denotes the energy absorbed within the molecules on expansion from the high pressures existing within the liquid to the low pressures existing in the vapor. The quantity of "e" is doubtless small compared to "L", that is most of the energy is required to overcome the attraction between the molecules, and but little in the expansion of the molecule itself. It may be stated that, in all probability, in so far as it concerns the overcoming of the attraction between molecules, the entropy of vaporization at the same concentration is the same for all normal liquids. If a liquid is associated, a third, and much larger quantity of energy is involved in the dissociation of the complex molecules into simpler ones. In such cases the total entropy of vaporization is distinctly greater than the normal values for a given concentration. Hildebrand considers that the low values of metals and also of gases boiling in the region of absolute zero are due to effects of the abnormally rapid changes of the specific heats.

The entropies of vaporization of the nitroanilines, toluidines and nitrotoluenes at temperatures at which the concentration of the vapor is .00507 moles per liter are given in Table I.

TABLE I

| Substance | Temperature—absolute at which C = .00507 moles/liter | Entropy of Vaporization Calories/degree |
|--------------------|---------------------------------------------------------|--------------------------------------------|
| Ortho nitroaniline | 480.9 | 16.0 |
| Meta nitroaniline | 500.4 | 15.7 |
| Para nitroaniline | 530.4 | 17.5 |
| Ortho toluidine | 401.6 | 16.4 |
| Meta toluidine | 405.1 | 15.6 |
| Para toluidine | 402.4 | 15.8 |
| Ortho nitrotoluene | 416.3 | 13.6 |
| Meta nitrotoluene | 427.2 | 14.0 |
| Para nitrotoluene | 431.5 | 13.9 |

It will be noticed that the toluidines and nitroanilines give values for the entropy of vaporization which are much higher than 13.8, which Hildebrand considered the normal value. Therefore, in all probability these compounds form associate or polar liquids. This is not the case with the nitrotoluenes which may be considered to be practically non-polar liquids.

It may not be too much to assume that there could be a relationship between the entropies of substances and their electrical structure, since, as is known, the heat of vaporization and association, dependent upon the polarity of the molecule, are related to its electronic structure. From a thermodynamic consideration it is evident that the entropy, association and heat of vaporization are very closely related. Therefore, a consideration of the electronic structure should, qualitatively, at least, interpret the relationship of the entropies of polar and non-polar compounds.

At the present time there exists no absolute means, or even quantitative relative means of expressing association. The order of association of various compounds can be arrived at through a consideration of their entropies of vaporization (also from the dielectric properties), but a compound may be twice as much associated as another and yet only be a few calory per degree higher in entropy. Yet, while not a measure of the association, the entropy of vaporization does offer a valuable means for comparing the association of various compounds. Hildebrand has shown that all non-associated compounds exhibit the same entropy of vaporization when the concentration of their vapors are the same. This rule is valid even to the critical temperature, for at this temperature the heat of vaporization is zero and the entropy of vaporization for all substances is zero and the entropy of vaporization for all substances is zero at their critical temperature. If the entropies of a series of compounds be compared at the same vapor phase concentration their relative association will be apparent. This is shown in Table I for the nine compounds under discussion.

The Molecule and its Electronic Structure

There are several electric conceptions of the structure of molecules, many of which have had to be radically modified or entirely discarded. The theory of chemical union as is now generally accepted is based on the Bohr conception of the atom under conditions defined by the quantum theory. The chemical aspect of the atom has been amplified by Kossel, Lewis, Langmuir, Stieglitz, Lowry, and Kharasch. However, as applied, there is the polar conception and the partial polar conception. In the polar conception, which is now rather limited to the field of inorganic chemistry, the bonding pair of electrons in a molecule are held by one atom or the other, depending upon which is the negative. In the partial polar conception the atoms comprising the molecule share the bonding pair (or pairs in the case of unsaturated compounds) of electrons between them, the position of the shared electrons shifting toward one side or the other dependent to the relative negativity or positivity of the atoms or groups. Thus it may be seen that there is really no fundamental difference between the polar, non-polar, and partial polar bond, but merely one of degree. If the bonding pair of electrons be held midway between two atoms the bond is of the typical co-valent or non-polar type; if the bonding pair is shifted so that one atom obtains exclusive possession of the electron pair the valency is of the electrovalent or polar type; while if the electron pair is not held by one or the other atom and not exactly midway between, the valence is partially polar in character. According to Dr. Rideal the gradation between polar and non-polar linkage due to a shift in the orbits of bonding or shared electron pairs takes place in quantumized stages.

In the case of the double bonding pair of electrons in the unsaturated compounds there is quite a distinction between the two pairs of electrons. One of these pairs of electrons is assumed of the non-polar type, that is, takes a position midway between two atoms, while the other pair of electrons is a partial polar type which can take up any position between the two atoms and its position will be determined by the relative negativity of the two atoms. This conception was developed by Lowry,¹⁶ and Lapworth and Robinson.¹⁷

If one should consider a saturated hydrocarbon, for instance, ethane; being a non-polar compound the bonding pair of electrons would be midway between the carbon atoms. Now if one should introduce a negative group like chlorine into the molecule, the bonding pair of electrons of the carbon and chlorine would be displaced towards the chlorine atom; and the electron pair between the two carbon atoms would be shifted away from the carbon atom attached to the halogen. That this is the direction in which the displacement takes place may be made evident by considering ethylene; in this compound the electrons forming the two bonding pairs are somewhere midway between the two carbon atoms. If the chlorine derivative of this compound—vinyl chloride—be considered, the position of the extra bonding pair of electrons between the two carbon atoms can be easily ascertained by treat-

¹⁶ Lowry: *J. Chem. Soc.*, 123, 822 (1923).

¹⁷ Lapworth and Robinson: *Trans. Faraday Soc.*, 19, 505 (1923).

ing this compound with a halogen acid. Upon treating vinyl chloride with hydrochloric acid, ethylidene chloride (unsymmetrical dichloroethane) is formed, showing that the bonding electrons shifted away from the carbon atom to which the chlorine is attached, and caused the other carbon atom to assume a relatively electro-negative condition since the positive hydrogen of the hydrochloric acid became attached to this carbon atom. This conception has been used by Kharasch, Stieglitz and others to explain many organic reactions.

A survey of the existing literature on electronic structure revealed but little on the electronic configuration of the benzene molecule. There have been several presentations on the electrical structure of benzene considering it from an electrostatic conception. Lowry,¹⁶ Holleman,¹⁸ Vorländer,¹⁹ Kermack and Robinson,²⁰ Lapworth²¹ and others, however may have had an electronic conception in mind, but did not publish anything that could be so considered.

However, there are a few investigators who consider benzene and its derivatives from the electronic conception of valence. Notable amongst these are Huggins²² and Crocker.²³

Huggins considers the benzene grouping in the light of Korner's²⁴ centroid structure and briefly reviews the present evidence for and against this structure which is based, to a large extent, on the conjugation hypothesis introduced by Erlenmeyer, Jr.²⁵ This structure agrees well with many properties of benzene especially its X-ray crystal structure. The principal objection to this structure is that it necessarily postulates that ortho and meta disubstituted benzene derivatives should be optically active and as yet no indication of this has been noted though much investigation has been instituted on this problem. Several investigators attempted a separation of the optically active forms by means of bacteriological means, but all their results were negative. Some of the workers on this phase were LeBel,²⁶ Lewkowitz,²⁷ Meyer and Luhn.²⁸ However, Huggins does not consider this sufficient proof against this conception and makes the rather interesting statement that "The objections raised to it are invalid or inconclusive," basing this on the consideration that the optically active isomers could be separated if the proper conditions were known and on the assumption that if they were separated they would rotate the plane of polarized light very little or not at all. Nevertheless the Korner centroid structure,²⁴ which consists essentially of six carbon tetrahedra having

¹⁶ Holleman: "Die direkte Einführung von Substituenten in der Benzolkern" (1910).

¹⁹ Vorländer: Ber., 52, 263-283 (1919).

²⁰ Kermack and Robinson, J. Chem. Soc., 121, 427 (1922).

²¹ Lapworth: Memoirs Manch. Phil. Soc., 64, 1 (1920); J. Chem. Soc., 121, 416 (1922).

²² Huggins: Science, 55, 674 (1922) J. Am. Chem. Soc., 44, 1607 (1922).

²³ Crocker: J. Am. Chem. Soc., 44, 1618 (1922).

²⁴ Korner: Gazz., 4, 444 (1874).

²⁵ Erlenmeyer: J. Ann. 316, 71 (1901).

²⁶ LeBel: Bull., (2) 38, 98 (1922).

²⁷ Lewkowitz: J. Chem. Soc., 53, 781 (1888).

²⁸ Meyer and Luhn: Ber., 88, 2795 (1895).

their bases all in one plane and their apexes alternately above and below this plane, does give quite a clear interpretation of the structure and it has been shown that the dimensions are almost exactly those corresponding to graphite. Huggins devotes very little of his discussion to the consideration of the electronic structure, which he considers to consist of six electrons around the center of each tetrahedron and two at each corner of the six hexagon formed by the six tetrahedrons making up the benzene nucleus. However, no evidence is given for this electronic structure and it is not discussed or applied.

Crocker's²³ conception deals with the benzene configuration from a strictly electronic viewpoint. His views agree extremely well with those of Kharasch and Stieglitz and brings the views of Lewis, Langmuir, Conant, and Parson into close agreement. His view may be briefly summarized in this manner—there is a ring of six carbon atoms, each singly bonded, by means of pairs of electrons, to its neighbor on either side, and to hydrogen. The remaining six electrons are placed between the carbons in the plane of the ring thus forming an octet for each carbon atom. Substituents of the hydrogen would cause a shifting in the position of these latter six "aromatic" electrons. The direction and degree of this shift, depends on the electrical nature of the substituent and Crocker considers this shift of the aromatic electrons to be mechanically the same as the shift of the electrons in the unsaturated hydrocarbons as in the illustrative example (ethylene) in the preliminary consideration; i.e., if any one of the aromatic electrons moves from its position midway between the carbon atoms, the electrical equilibrium of the system is disturbed and the others must move in such a manner as to restore it. Thus if a positive group, such as the amino group, which repels the paired electrons, to be introduced into the nucleus to form aniline, the aromatic electrons would be attracted towards the 3 and 5 positions and repelled at the 2 and 4 positions. If a negative group such as the nitro group, that strongly attracts the electron pair be introduced into the nucleus to form nitro benzene the electrons will be attracted towards positions 2, 4 and 6 and repelled at the 3 and 5 positions. Crocker considers that substitution is possible only at those positions where the hydrogens are lightly held, that is, the position where the electrons are repelled. It is seen how well this conception explains the reason why benzene derivatives containing negative group—which causes repulsion of electrons at the meta positions are readily substituted in this position while in the case of compounds like aniline, substitution takes place at the orth and para positions, since it is at these positions that the positive amino group causes the electrons to be shifted away from the nucleus. Holleman²⁴ has very ably discussed the relation of the various groups to their directive powers in the benzene derivatives and Schwalbe²⁵ has made quite a complete compilation of the data pertaining to this.

This conception seems to give the clearest view of the operation of the forces about the molecule and is in very fine agreement with the known facts.

²³ Holleman: "Substituenten in den Benzolkern", (1910).

²⁵ Schwalbe: "Benzol Tabellen" (1903).

If these deductions are now expanded upon and the conception of a type of co-valence introduced this view of the molecule of benzene and its derivatives may be applied to the interpretation of facts with which it appears, at first, to have no connections.

As was previously mentioned, it seems quite reasonable to postulate that entropy, molecular association and electronic structure may be interrelated. The association of molecules takes place only in the case of polar molecules, that is in those molecules in which the electrical charges are not balanced or the electric moment is not zero. It is seen that this is also one of the conditions under which compounds exhibit co-ordination values. Thus, it has been suggested by Huggins and by Lewis³¹ that the reason for the association of water, ammonia, hydrofluoric acids and similar compounds can be attributed to hydrogen exhibiting a secondary valence or co-valence under the conditions of the great electric or magnetic moments that exist in the molecules of these substances. This suggestion of bivalent hydrogen has been applied by Latimer and Rodebush³² in the interpretation of the association and structure of ammonium hydroxide. As will be indicated in the succeeding treatment on this subject, the co-valency of the hydrogen may be the factor causing the association of the organic molecules, although it is not necessary to postulate that this bivalent form of hydrogen, if it does really exist, is essential to the explanation of the observed phenomena. It is merely noted as a possible factor in the future development.

Electronic Structure of the Compounds studied

In the substances considered in this discussion there are three groups of atoms, the nitro, the methyl, and the amino group, that enter into all the isomeric relations to each other that are possible in their disubstituted benzene derivatives. These may be considered in terms of relative basicity. In the following treatment, a group will be considered as negative if, when joined to the hydroxyl group, it allows the hydrogen of the hydroxyl to be reactive, such as the nitro or sulphonic acid group, NO_2OH , $\text{SO}_2\text{H.OH}$. Conversely, positive groups such as amino when joined to the hydroxyl allow the whole hydroxyl group to react. It is apparent that from this consideration the methyl group is very weakly negative, since, although in methyl alcohol the hydroxyl may be readily split off, as by the action of hydriodic acid, yet it can in addition have the hydrogen of the hydroxyl replaced by much more positive substances such as sodium and potassium.

From the present knowledge of the electronic structure of benzene it may be represented as in A, Fig. 1. This is essentially that proposed by Crocker³³.

Here the small dots represent the normal bonding pair of electrons between the carbon atoms and are considered to be stationary; the large dots the aromatic or polar electrons, which are the ones that shift under the influence of various substituents; and the small circles represent the bonding pair of electrons between the hydrogen and carbon atoms. These latter electrons

³¹ Lewis: "Valence and the Structure of Atoms and Molecules," 109. (1923).

³² Latimer and Rodebush: J. Am. Chem. Soc., 42, 1419 (1920).

shift in their positions relative to the character of the substituent and the position of the aromatic electrons. For convenience of illustration the benzene nucleus will be employed as shown by (B) in Fig. 1, where the large black dots represent the aromatic electrons and the position of the hydrogen-

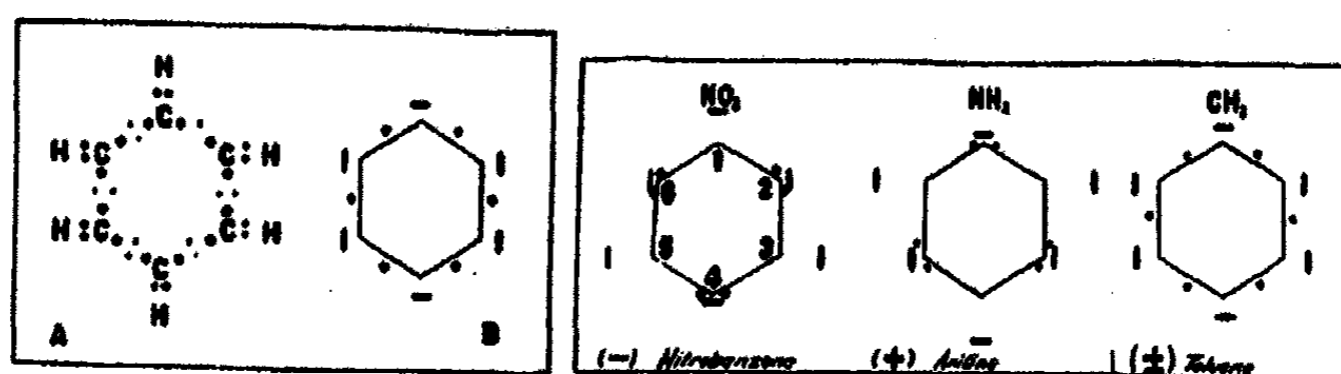


FIG. 1

FIG. 2

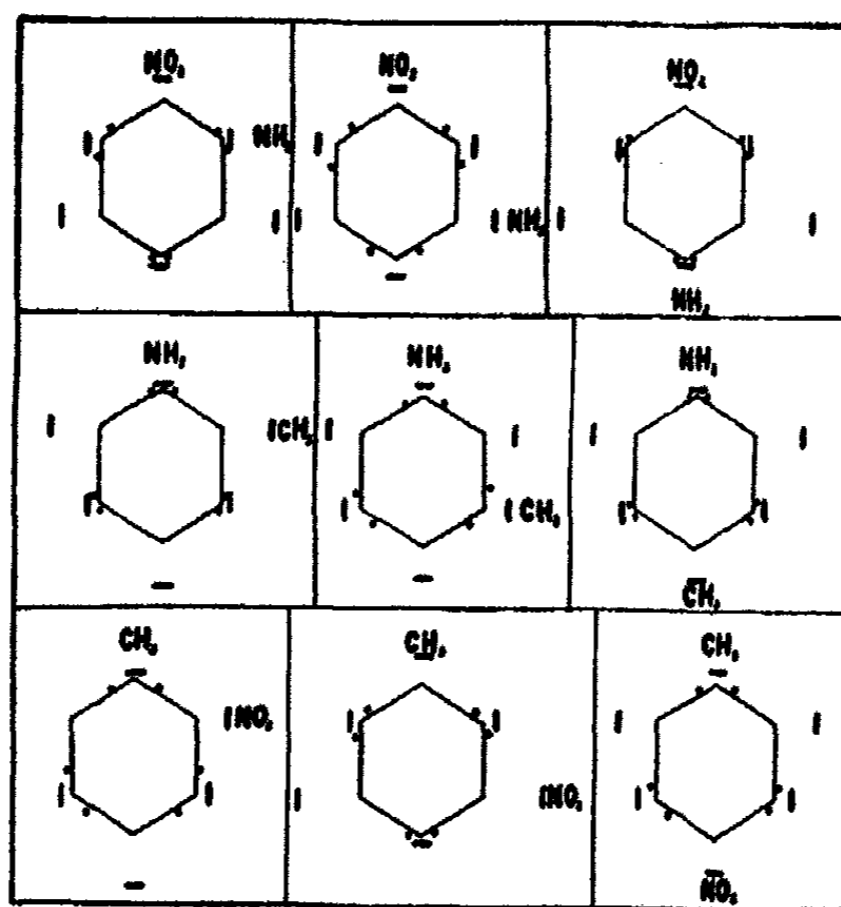


FIG. 3

carbon bonding electrons are represented by the small bars at the corners of the hexagon by which is to be comprehended the carbon nucleus and the normal bonding electron pairs. The hydrogen symbol will be omitted.

The effect of the type of substituent group on the aromatic electrons of the benzene configuration has been considered in the earlier part of this discussion. These structures may be illustrated as in Fig. 2. It will be apparent from these figures that the nitro group being a strongly negative group attracts the hydrogen bonding pair of electrons (represented by the bars) towards itself, thus causing the above configuration; conversely the amino group being strongly positive repels its bonding pair of electrons causing the aromatic electrons of the 2 and 6 position to approach the 1 position and in-

ducing the electronic arrangement presented above. In toluene the methyl group is practically neutral or slightly negative and the differences between it and the other configurations are but of degree.

In the compounds chosen for this investigation, all the combinations of the above structures are involved. Besides having a definite effect on the aromatic electrons, each group has a profound influence on the effects of the other group present, which depends both on the type of group and its position in the benzene nucleus. The nine compounds studied are represented in Fig. 3 on the basis of the interpolated conception of the electronic structure introduced in this treatment. An attempt has been made to illustrate the degree of repulsion and attraction of the bonding pairs of electrons by means of the variations in the distances from the nuclei of the bars employed to represent the relative positions of the hydrogen-carbon bonds, and of the aromatic electrons. These are to be considered strictly of a qualitative nature and are to some degree exaggerated, for purposes of illustration the relative effects on the electronic configuration caused by the complex inter-effects of the two substituent groups.

In the nitroanilines there is a strongly positive group and a strongly negative group present. As will be evident from the illustrations in Figs. 2 and 3, the amino group in the ortho and para position to the nitro group would act in such a mode as to greatly exaggerate the conditions already present, that is the electrons would be attracted very powerfully to the 2, 4 and 6 position and very strongly repelled at the 3 and 5 positions. However, in the case of the meta isomer, it will be apparent that the effect of the amino group is opposed to that of the nitro group because the nitro group is attracting the paired electrons away from the nucleus while the amino group is forcing them towards the nucleus. Since this condition exists, the effects of the nitro group will be materially diminished and the configuration altered to one that more nearly approaches that of benzene than that of nitro-benzene or aniline.

There are some differences between the ortho and para configuration that are of importance to note. While the amino group in either the ortho or para position to the nitro group tends to greatly increase the effects caused by the nitro group there are differences in degree of this effect between them. The amino group in the para position has a more profound influence in exaggerating the nitrobenzene structure than the ortho amino group. This difference may be accounted for by two considerations. The first, is that the ortho amino group, due to its stereochemical position has a greater effect on the reactive repelled electrons in the 3 position than it has on those in the 5 position and in its effect on the 5 position it is to some extent hindered through having the nitro group in an intermediate position, on one side, between the amino group and the 5 position. The second consideration is a purely chemical one. It has been shown by several investigators, notably Baly, Edwards, and Stewart,³³ Baly, Tuck and Marsden,³⁴ Hantzsch³⁵ and Kharasch, Lom-

³³ Baly, Edwards and Stewart: *J. Chem. Soc.*, 89, 517 (1906).

³⁴ Baly, Tuck and Marsden: *J. Chem. Soc.*, 97, 581 (1910).

³⁵ Hantzsch: *Ber.*, 43, 1668 (1910).

men, and Jacobsohn,³⁶ that there is marked tendency for the nitro group and amino group, when in the ortho or para positions to each other or to other reactive groups, to react to form quinone derivatives of the nitronic acid and quinone-dioxime types. This effect will be subsequently discussed. Now it is apparent that in a reaction of this nature, which can be considered as forms of neutralization, the effects of the substituents on the electronic configuration would be such as to cause a change of the electronic arrangement in the direction of the non-polar type of compound; also it is apparent that in an intramolecular rearrangement or reaction, (may also be considered as an intermolecular reaction), the reacting groups would have a much greater tendency to react if they are adjacent to each other as in the orthonitroaniline, than if they were relatively greatly displaced as in the para derivative. These two considerations are believed to be sufficient to account for the difference in electronic configuration and therefore the relative association between the ortho and para nitroaniline. In fact it is easily conceived that the rearrangement producing a partial electrical neutralization in the ortho derivative, may be so great as to cause this compound to, electronically, approach quite close to the meta arrangement.

Electronic Structure and Molecular Association

From the consideration of the previously discussed hypothesis of Huggins and Lewis, it is conceivable that the greater the electronic moment of a molecule, that is, the more labile its electronic charges, the more polar it becomes and therefore the more associated. In the nitroanilines, as is evident from this postulate, the para isomer is very much more polar than the ortho or meta, and the ortho nitroaniline is more polar than the meta. Since the polarity is the cause of association of molecules, the higher the polarity the greater the association. As was explained in the preceding section, the association of a molecule is related to the entropy of vaporization of that substance. Therefore, it may be stated, that the polarity and entropy of a molecule are directly related.

Reference to Table I indicates that the entropy of vaporization of the isomeric nitroanilines are in fine agreement with the conclusions of the preceding discussion of their relative polarities. As is required by the electronic conception that is advanced in this treatment, the para nitroaniline should have a far greater entropy of vaporization than the ortho and meta isomers since its polarity is so much greater; likewise since the polarities of the ortho and meta nitroanilines are not greatly dissimilar the values for the entropies of vaporization are relatively close together for these two compounds. This agreement gives very substantial indication that the premises assumed for the structure of these compounds are correct.

In the toluidines, there are present a strongly basic or positive group and a very weak negative group. As would be supposed the methyl group has a relatively small though appreciable effect. Considering the electronic structure as that of aniline, it is readily noted that a negative group would tend to

³⁶ Kharasch, Lommen and Jacobsohn: *J. Am. Chem. Soc.*, 44, 793 (1933).

intensify the polarity of the initial electronic configuration if it were in the ortho or para position. Therefore, the ortho and para toluidines should be more polar, hence more associated, and should have a higher entropy of vaporization than the meta.

In the ortho toluidine the effect of the methyl group on the electrons of the 6 position, is transmitted and increased by the amino group thus causing the electrons of the 6 position to be somewhat more displaced than those of the 4 position. In the para toluidine the two electron pairs ortho to the amino should be equally repelled from the nucleus; thus it is evident that the ortho toluidine should be more polar than the para compound and therefore have a higher entropy of vaporization. As may be ascertained from the table of the entropies of vaporization, the above conclusions are justified.

The precepts, as presented for the toluidines and nitroanilines, should apply to the nitrotoluenes as well. The validity of this is observable from the following consideration and from the representation of these compounds in Fig. 3. Since both the nitro and the methyl group are negative it will be at once evident that when they are in a meta position to each other the electronic configuration originally present in the nitrobenzene will be somewhat intensified and therefore the meta nitrotoluene will be the most polar mononitrotoluene. Since the effect on the electron displacement in the nitrotoluenes is due almost entirely to the nitro group the methyl group in the para position will have little or no effect on the electron displacement of the positions meta to the nitro group and therefore the para nitrotoluene is but slightly less polar than the meta isomer. In the ortho nitrotoluene the effect of the nitro group is diminished by having to be exerted through the methyl group which is in a position such as to oppose the forces of the nitro group, at least for one position (ortho to the methyl). As in the case of the ortho nitroaniline there may be some intramolecular rearrangement or reaction. This will subsequently be referred to. The nitrotoluenes which, it is to be recalled, are polarized but slightly if at all, are nevertheless in accord with the principles that are applicable to the other compounds.

Thus it is evident that the electronic structures of these compounds are related to their association and polarity and the sequence and relative degree of this association is in agreement with the values derived from experimental evidence.

Effect of Intramolecular Reactions

From a consideration of the electronic configuration alone, one would deduct that the ortho nitroaniline and the ortho nitrotoluene would be more highly associated and have a higher entropy than they actually exhibit. As has been indicated the lower degree of polarity of these compounds is thought to be due to some intramolecular reaction. There is at the present time much speculation on this type of reaction and the constitution of these intramolecularly condensed compounds that are known as "meriquinoids." These were first observed by Wurster²⁷ in 1879 and then studied by Bernthsen,²⁸

²⁷ Wurster: Ber., 12, 1803, 1807, 2071 (1879); 13, 3195, 3217 (1880).

²⁸ Bernthsen: Ann., 230, 162 (1885); 251, 11, 49, 82, (1889).

Willstätter, and Pfannenstiel,³⁹ and Willstätter and Piccard,⁴⁰ who concluded that these compounds were a class of quinone derivatives of a semiquinoneimide type. It has been suggested by Kehrman,⁴¹ Kaufmann,⁴² and Meyer⁴³ that the two reactive components exist in a condition of dynamic equilibrium with reference to each other which they call "isorropesis" or the make-and-break in the linkages of the residual valencies. While this term is usually applied to an intramolecular condition, it may be extended to include an intermolecular condition such as is represented in the recurrent making and breaking of linkages between different molecules.

It may therefore be safely assumed that in ortho nitroaniline and probably ortho nitro-toluene there is a great tendency for an isorropesic condition to exist and from a consideration of their electronic arrangements and their entropies of vaporization one may reasonably presuppose that such condition does exist.

Summary

A relationship between the electronic configuration and association as derived from vapor pressure measurements is shown to exist. This has been applied in the interpretation of the variations in the entropies of vaporization of the isomeric nitroanilines, mononitrotoluenes and toluidines. The significance of the relations has been considered.

Washington, D. C.
1927.

³⁹ Willstätter and Pfannenstiel: Ber., 38, 2244 (1905).

⁴⁰ Willstätter and Pfannenstiel: Ber., 38, 2244 (1905).

⁴¹ Kehrman: Ber., 41, 2340 (1908); see also p. 1458.

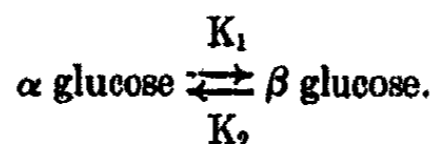
⁴² Kaufmann: "Die Valenzlehre," p. 510; also Ber., 42, 4324 (1909).

⁴³ Meyer: Ber., 41, 2568 (1908); 42, 1149 (1909); 43, 157 (1910).

MUTAROTATION IV. CONSECUTIVE REACTIONS IN THE MUTAROTATION OF GLUCOSE AND GALACTOSE

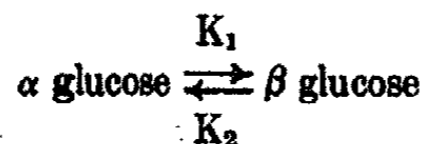
BY FREDERICK PALLISER WORLEY AND JOHN CLARK ANDREWS

Experimental investigation of the mutarotation of glucose has hitherto failed to afford any definite indication that the process is other than the direct attainment of simple equilibrium between α glucose and β glucose, represented by the equation



The reaction appears to be strictly unimolecular from each end, but since the velocity is enormously affected by alkalies and to a smaller extent by acids, the catalyst should appear on each side of the equation, the reversible reaction being probably bimolecular. In the polarimetric method of following the course of the change, optical rotations of the substances present are taken as proportional to their concentrations. It is found that the rate of change of rotation at a given time is proportional to the difference between the rotation at this time and at equilibrium, this ratio being the velocity coefficient. It can easily be shown that this should be the case if the reaction is a reversible unimolecular change or a reversible bimolecular change in which the second reactant on each side of the equation remains constant. Furthermore, the velocity coefficient of mutarotation of α glucose and β glucose determined in this manner under similar conditions should be the same, viz. $K_1 + K_2 = K$.

If in the reversible reaction



the initial concentrations of α and β glucose be a and o respectively, and if the amounts of α glucose converted to β glucose at time t and at equilibrium be x_t and x_∞ respectively, then at time t

$$dx/dt = K_1(a - x_t) - K_2x_t$$

at equilibrium

$$K_1(a - x_\infty) = K_2x_\infty$$

$$x_\infty = \frac{K_1 a}{K_1 + K_2}$$

at time t

$$\frac{dx/dt}{(a - x_t) - (a - x_\infty)} = \frac{dx/dt}{x_\infty - x_t}$$

$$\begin{aligned}
 &= \frac{K_1(a-x_t) - K_2x_t}{\frac{K_1a}{K_1 + K_2} - x_t} \\
 &= K_1 + K_2
 \end{aligned}$$

Hence in the polarimetric method of following the mutarotation

$$K_1 + K_2 = \frac{1}{t_2 - t_1} \log \frac{(\alpha_1) - (\alpha_\infty)}{(\alpha_2) - (\alpha_\infty)}$$

in which α_1 , α_2 and α_∞ are the rotations at t_1 , t_2 and t_∞ .

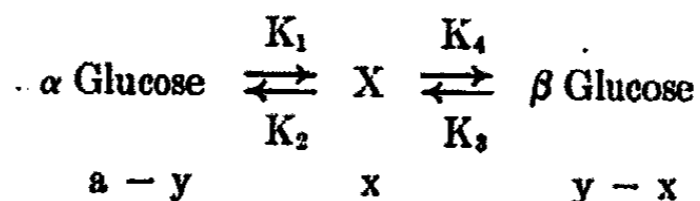
The velocity constant as usually determined should thus be $K_1 + K_2$ in the case of both α glucose and β glucose.

It has been amply shown that the reaction over the very large portion investigated is strictly unimolecular and that the velocity coefficients of mutarotation of α glucose and β glucose are identical under similar conditions.¹

It has also been shown that if α and β glucose be mixed in the proportion calculated to be present at equilibrium both in the case of water and of methyl alcohol, on the assumption that the reaction is expressed by the above simple equilibrium, and dissolved in the respective solvents, there is no detectable change of rotation after dissolution² indicating that there is no third substance present at equilibrium capable of detection by the physical methods employed.

These considerations, however, do not eliminate the possibility of mutarotation proceeding in two, or more stages, but show that if an intermediate substance is formed, the rate of its transformation into α and β glucose must be very much greater than that of its formation. If the velocity of transformation were a large multiple of that of the reverse change, there would be only a small percentage of the sugar in the intermediate form at equilibrium, and, since the physical methods employed in the mixture experiments are dependent on the *difference* between the physical properties of the intermediate form and those of the mixture of α and β glucose from which it is formed, this small amount of a third substance would not be detected in the experiments. Its formation should, however, be indicated by the course of the reaction at the beginning of mutarotation.

If we assume that starting from α glucose, the original concentration is a and that at time t the amount left is $a - y$ and the amount of the intermediate substance X formed is x , the concentration of β glucose will be $y - x$ according to the equation.



¹ Roux: Ann. Chim. Phys., 30, 422 (1903); Hudson and Dale: J. Am. Chem. Soc., 39, 320 (1917); Andrews and Worley: J. Phys. Chem., 31, 882 (1927).

² Roux: Ann. Chim. Phys., (7) 30, 422 (1903); Riiber: Ber., 56, 2185 (1923); Andrews and Worley: J. Phys. Chem., 31, 1880 (1927).

From the fact that there is no detectable amount of an intermediate substance present at equilibrium, it follows that $K_2 + K_4$ must be large in comparison with K_1 and K_3 . Let $K_1 + K_3 = k$. The rate of formation of X is given by

$$\begin{aligned} dx/dt &= K_1(a - y) + K_3(y - x) - (K_2 + K_4)x \\ &= K_3(a - x) + k(a - y) - (K_2 + K_4)x \end{aligned}$$

If $k = 0$, dx/dt becomes zero, x reaching a maximum when

$$K_3(a - x) = (K_2 + K_4)x$$

thereafter x remains constant during the remainder of mutarotation until equilibrium is attained.

If k has a positive or negative value, dx/dt becomes zero and x reaches a maximum when

$$K_3(a - x) + k(a - y) = (K_2 + K_4)x$$

If k is positive x will reach a maximum and thereafter decrease as $a - y$ decreases until equilibrium is reached. If, however, k is negative x will increase as long as $a - y$ decreases, that is, during the whole course of mutarotation.

Consider first the simpler case when $K_1 = K_3$. In the mutarotation of either α glucose or β glucose, the concentration of the intermediate substance will increase from zero to a maximum and thereafter be constant during the remainder of mutarotation, the concentration at maximum depending on the ratio of K_3 to $K_2 + K_4$. Accompanying the gradual increase in the concentration of the intermediate substance, whether we start from α glucose or β glucose, there will be a corresponding increase in the rate of formation of the other isomer until the maximum amount of the intermediate form is present. There will thus be initially an apparent retardation in the rate of mutarotation which will be the same whether we start with α glucose or β glucose.

If K_1 is not equal to K_3 , there will also be an initial retardation, but the effect in the case of α glucose will be somewhat different for that in the case of β glucose. If $K_1 > K_3$, the retardation with α glucose should be more pronounced, but of shorter duration than with β glucose and vice versa.

In the polarimetric method of following the course of mutarotation, an additional complication is introduced by the optical activity of the intermediate substance. The retardation will be modified according as the intermediate substance has a high or a low rotation. If high, the retardation in the case of α glucose will appear more pronounced, while in the case of β glucose, it may be diminished, obscured, or possibly converted into an apparent acceleration. In the light of the above analysis of the problem, various initial effects may be expected according as K_1 is greater than, equal to, or less than K_3 , and according as the intermediate substance has a high or low rotation.

In the case of galactose, Riiber¹ followed the course of mutarotation by methods dependent on (1) the change in volume of the solution and (2) the

¹ Ber., 59, 2266 (1926).

change in refractivity as well as by (3) the polarimetric method. By the dilatometer method he found that in the initial stages of mutarotation of α galactose the reaction departed considerably from the unimolecular nature of the subsequent part of the mutarotation. There was, however, no observable departure in the case of β galactose. He assumed the formation of a third or intermediate form of galactose and by an elaborate mathematical investigation, arrived at the four velocity constants and the proportions of the three forms present at equilibrium. By the refractometric method, a slight and doubtful divergence from the subsequent uniform unimolecular nature of the reaction was observed in the initial stages. By the polarimetric method no departure was indicated. In the case of the glucose, Riiber found no evidence for the existence of an intermediate form, the reaction appearing regular from the beginning when treated as a simple unimolecular balanced action.

Mutarotation of Glucose and Galactose at 0°C

It is possible that at 25° any retardation in the mutarotation of glucose may occur only in the short interval after dissolving the sugar when the polarimetric readings are not taken or are discarded owing to the possibility of the temperature not having become constant. In order to examine the initial stages more minutely, we have carried out experiments at 0°C with α and β glucose and α and β galactose in aqueous solution, the velocity of mutarotation being very much less at this temperature than at 25°, and any initial retardation correspondingly protracted.

The polarimetric tube was imbedded in crushed ice in a box considerably longer than the tube. Extension tubes attached to the polarimetric tube passed through holes in the box. The sugar and the water were mixed at 0°C and quickly transferred to the polarimetric tube imbedded in the crushed ice. Readings were taken at frequent intervals after mixing and afterwards at longer intervals. In Tables I-IV are given the results of four typical experiments made with α and β glucose and α and β galactose respectively. Each rotation is the mean of five readings taken at intervals of ten seconds.

The results of the above four experiments are shown graphically in Figs. 1 to 3. In Figs. 1 and 2 the observed rotations are plotted as ordinates and the times as abscissae, the curves thus representing the course of mutarotation as indicated by the change in optical rotation. In the case of both α and β galactose (Fig. 1) there is an initial flattening of the curve indicating an initial retardation which is more pronounced in the case of the β sugar. In the case of glucose (Fig. 2) there is an initial flattening or retardation in the case of α glucose, but an initial acceleration in the case of β glucose.

In Fig. 3 the logarithms of the differences between the specific rotations at the various times and the specific rotation at equilibrium are plotted as ordinates against the times as abscissae. In order to plot the curves in one diagram, the logarithms of α galactose and α glucose have been diminished by 0.10 and 0.17 respectively and those of β galactose increased by 0.03 throughout. If the velocity of mutarotation be in accordance with the re-

MUTAROTATION

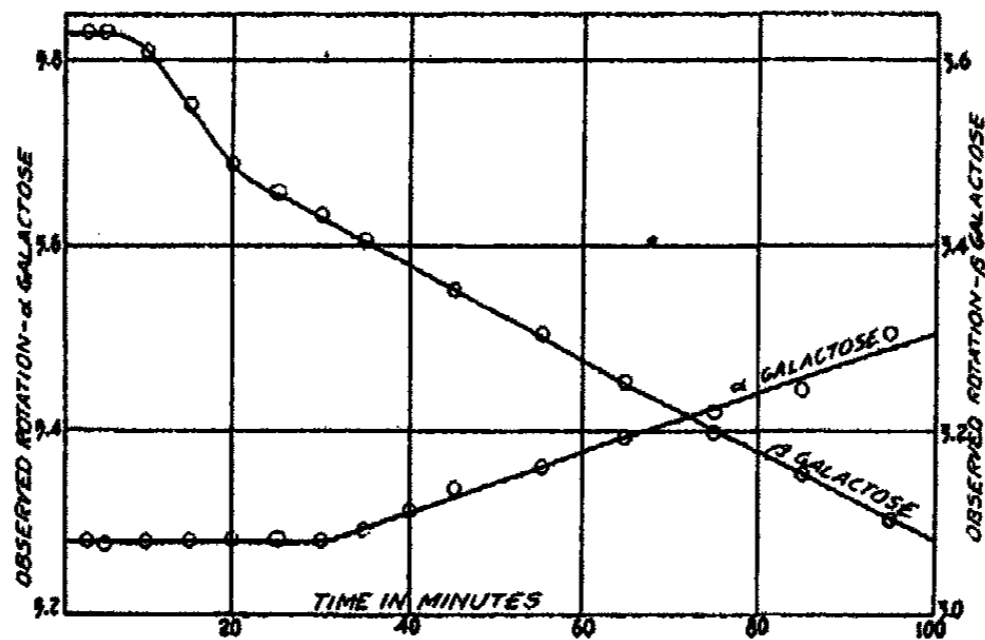


Fig. 1

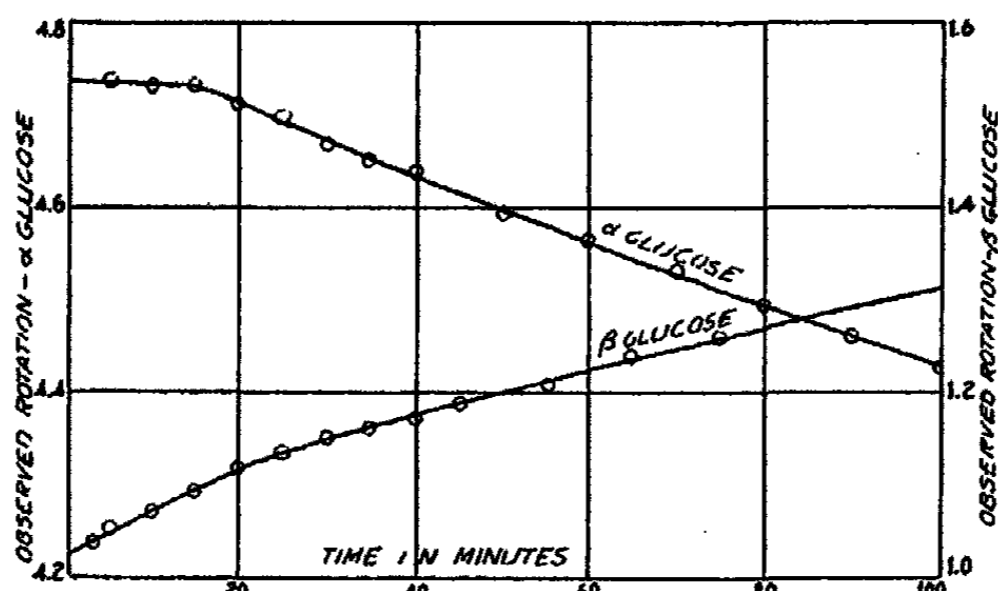


Fig. 2

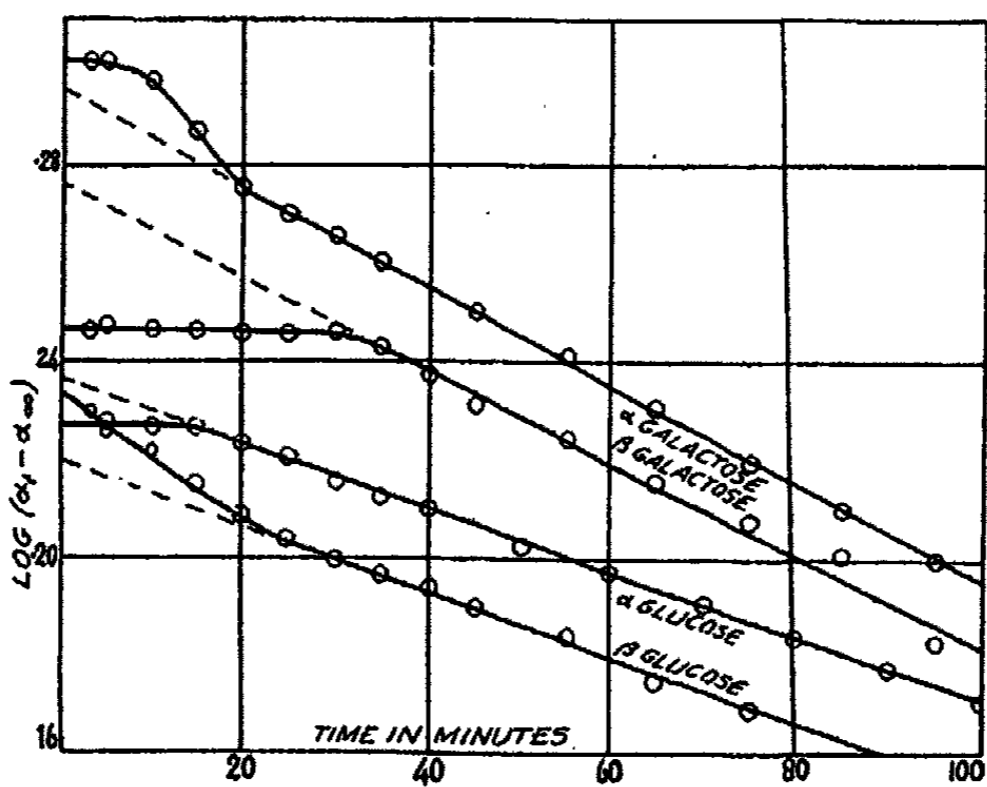


Fig. 3

TABLE I
 α Glucose
0.4793 gms. in 25.100
gms. water
 $d_4^0 = 1.00580$

| Times | Observed Rotation |
|----------|-------------------|
| 5 min. | 4.736 |
| 10 | 4.730 |
| 15 | 4.730 |
| 20 | 4.710 |
| 25 | 4.696 |
| 30 | 4.666 |
| 35 | 4.650 |
| 40 | 4.636 |
| 50 | 4.592 |
| 60 | 4.564 |
| 70 | 4.530 |
| 80 | 4.494 |
| 90 | 4.460 |
| 100 | 4.426 |
| 130 | 4.322 |
| ∞ | 2.236 |

TABLE III
 α Galactose
0.4378 gms. in 25.100
gms. water
 $d_4^0 = 1.00534$

| Times | Observed Rotation |
|----------|-------------------|
| 3 min. | 5.830 |
| 5 | 5.830 |
| 10 | 5.808 |
| 15 | 5.750 |
| 20 | 5.686 |
| 25 | 5.656 |
| 30 | 5.632 |
| 35 | 5.604 |
| 45 | 5.550 |
| 55 | 5.504 |
| 65 | 5.452 |
| 75 | 5.398 |
| 85 | 5.352 |
| 95 | 5.304 |
| 105 | 5.264 |
| 115 | 5.224 |
| 125 | 5.180 |
| ∞ | 3.310 |

TABLE II
 β Glucose
0.5771 gms. in 25.100
gms. water
 $d_4^0 = 1.00819$

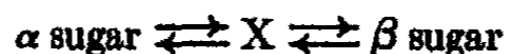
| Times | Observed Rotation |
|----------|-------------------|
| 3 min. | 1.136 |
| 5 | 1.152 |
| 10 | 1.170 |
| 15 | 1.192 |
| 20 | 1.216 |
| 25 | 1.234 |
| 30 | 1.250 |
| 35 | 1.260 |
| 40 | 1.270 |
| 45 | 1.286 |
| 55 | 1.306 |
| 65 | 1.338 |
| 75 | 1.358 |
| 105 | 1.430 |
| 135 | 1.490 |
| ∞ | 2.834 |

TABLE IV
 β Galactose
0.6251 gms. in 25.100
gms. water
 $d_4^0 = 1.00870$

| Times | Observed Rotation |
|----------|-------------------|
| 3 min. | 3.080 |
| 5 | 3.076 |
| 10 | 3.080 |
| 15 | 3.080 |
| 20 | 3.082 |
| 25 | 3.082 |
| 30 | 3.080 |
| 35 | 3.092 |
| 40 | 3.114 |
| 45 | 3.136 |
| 55 | 3.160 |
| 65 | 3.192 |
| 75 | 3.220 |
| 85 | 3.244 |
| 95 | 3.304 |
| 115 | 3.358 |
| 135 | 3.398 |
| 155 | 3.460 |
| ∞ | 4.726 |

quirements of a unimolecular balanced action, as has already been found to be the case during the greater part of the mutarotation, a straight line should be obtained, the slope of the line affording the value of the velocity coefficient. This method of expressing the results clearly shows the nature and duration of the initial divergence from the unimolecular character of the change obtaining during the subsequent mutarotation. In the case of α galactose the initial retardation is seen to be followed by an acceleration before the mutarotation becomes regular as expressed by the straight part of the curve, the initial divergence extending for about twenty minutes. In the case of β galactose, there is an apparent complete arrest of mutarotation for about thirty minutes, after which the action becomes normal. The slope of the two curves when they become straight lines is approximately the same, that for α galactose, however, being slightly the greater. In the case of α glucose, the retardation extends over about fifteen minutes before the curve becomes a straight line. The initial divergence in the case of β glucose is an acceleration extending for about twenty-five minutes, the subsequent straight part of the curve having the same slope as that of α glucose.

The possibility of the initial divergence being due to the temperature not having become constant has been considered, but although a portion of the divergence may be due to a temperature effect, it appears that such portion must be small in comparison with the total effect observed. Four or five experiments were carried out in each case and the general form of the curves for each sugar found always to be the same. We consider that the different characters of the initial divergences are to be explained principally by the magnitude of the rotation of the intermediate substance and by the relation of K_1 to K_3 . These results we regard as definite evidence against mutarotation being a simple unimolecular balanced action between the α and the β sugar. They appear to be in agreement with the requirements of an action which proceeds by the formation of an intermediate substance and represented by—



in which the rate of formation of X is very slow in comparison with the reverse changes. Although the possibility is not excluded of mutarotation proceeding in more than two stages with the formation of more than one intermediate substance, there is no evidence that more than one intermediate substance is formed, and it is reasonable to assume provisionally that one only is present. In the case of galactose, the more prolonged initial divergence from the uniformity of the subsequent course of mutarotation compared with that of glucose, considering also the greater speed of mutarotation of galactose, indicates that the difference between the rate of formation of the intermediate substance and the reverse changes is considerably greater in the case of glucose than in that of galactose, with the result that the amount of the intermediate form present during mutarotation and at equilibrium will be considerably greater for galactose than for glucose.

Temperature Coefficient of Velocity of Mutarotation

The velocity coefficients at 0°C and 25°C are given in Table V. The values at 0°C being the means of five determinations in the case of α glucose and α galactose and four determinations in the case of β glucose and β galactose.

| | 0°C | 25°C | $\frac{K_{25}}{K_0}$ |
|--------------------|---------|--------|----------------------|
| α glucose | 0.00073 | 0.0096 | |
| β glucose | 0.00073 | 0.0096 | |
| mean | 0.00073 | 0.0096 | 13.2 |
| α galactose | 0.00092 | 0.0134 | |
| β galactose | 0.00090 | 0.0134 | |
| mean | 0.00091 | 0.0134 | 14.7 |

From these results the velocity of mutarotation for a rise of 10°C is increased 2.8 times for glucose and 2.9 times for galactose. At 25° the initial divergence would be completed within the first two minutes after mixing. This accounts for the divergence not being detected at 20 or 25° by the polarimetric method.

In the mutarotation of glucose in methyl alcohol, since the rate is very much reduced, it should be possible to observe an initial divergence at 25°C corresponding to the divergence in aqueous solution at 0°C. An experiment carried out with α glucose in methyl alcohol at 25° C has shown a retardation extending over about an hour. We are investigating the initial mutarotation of β glucose in methyl alcohol. It is possible that the partial or complete "arrest" of mutarotation which has sometimes been observed¹ is to be explained in the same way as the initial divergence we have observed in the above experiments.

Summary

1. The mutarotation of α and β glucose and α and β galactose in aqueous solution has been examined by the polarimetric method at 0°C in order to investigate the initial stages of the action.

2. It is found that in each case there is an initial divergence from the subsequent uniform unimolecular nature of the change. In the case of α galactose, there is an initial retardation followed by an acceleration; in the case of β galactose mutarotation appears completely arrested for about thirty minutes. In the case of α glucose an initial retardation is observed and in the case of β glucose an initial acceleration.

3. It is claimed that these divergences show that mutarotation is not a simple unimolecular balanced action, but are in agreement with the requirements of an action proceeding in two stages with the formation of an intermediate substance, the different characters of the divergence being due to the magnitude of the rotation of the intermediate substance and the relative values of the velocity constants.

¹ Lowry and Richards: J. Chem. Soc., 127, 1385 (1925); Faulkner and Lowry: 1926, 1938.

4. The temperature coefficients of the velocity of mutarotation of glucose and galactose have been determined. The velocity constant for glucose is increased 2.8 times and for galactose 2.9 times for a rise of 10°C .

We desire to express our indebtedness to the Royal Society for a grant to one of us (F.P.W.) towards the cost of polarimetric apparatus, and to the N. Z. Department of Scientific and Industrial Research for a National Research Scholarship which enabled one of us (J.C.A.) to take part in the investigation.

*Auckland University College,
University of New Zealand,
August 20, 1927.*

NEW BOOKS

Colloids By H. R. Kruyt. Translated by H. S. van Klooster. 23 × 16 cm; pp. xi + 268. New York: John Wiley and Sons, 1927. Price: \$3.50. In the general introduction the chapters are entitled: preliminary consideration of colloidal systems; boundary phenomena; capillary electrical phenomena. Part II deals with suspensoids and the headings of chapters are: stability of suspension; charge and stability; constitution of the double layer; kinetics of flocculation; optical properties of suspensoids; properties of suspensoids from the kinetic point of view; formation of suspensoid sols; historical outlines of the development of the theory of suspensoids. Emulsoids are taken up in Part III with chapters entitled: general properties of emulsoids; stability of emulsoids; protein sols, osmotic phenomena; gels. There is a final chapter on special sols which constitutes Part IV.

In spite of the fact that dyeing—a typical adsorption process—may take a very long time at room temperatures and some minutes even at the boiling-point, Kruyt states definitely, p. 34, that adsorption equilibria are reached quite rapidly.

"Robert Marc has found that the adsorption of starch by powdered crystals is 90 per cent complete within a few seconds. In general, adsorption equilibria of this kind are established in a few minutes. Whenever we meet with an adsorption reaction that does not reach a final value within this period of time, we can be reasonably sure that it is not a simple one. For instance, in the adsorption of oxalic acid by charcoal, the condition reached after ten minutes apparently does not represent complete equilibrium since the concentration of the liquid continues to decrease, although very slowly, for several hours. Further investigations have shown that the adsorbed oxalic acid reacts with dissolved oxygen, and that this process is catalytically accelerated in the adsorption layer. This combination of adsorption and chemical reaction occurs frequently. Pure adsorption processes are characterized by a rapid attainment of the final state of equilibrium."

"The phenomena observed when a sol is flocculated by means of an electrolyte such as AlCl_3 agree well with the changes in boundary potential. When increasing amounts of AlCl_3 are added to a negatively charged sol of mastic, we notice that small concentrations cause flocculation, somewhat higher concentrations produce another stable sol of opposite sign, i.e., positively charged, while still higher concentrations bring about another flocculation. . . . We have, therefore, first a non-flocculation zone, next a primary flocculation zone, then another non-flocculation zone in which the sol has the opposite sign and, finally, a secondary flocculation zone.

"This phenomenon is designated as an *irregular series*. It will always occur when the potential-lowering effect of the cation is far in excess of the potential-raising effect of the anion. This lowering effect may be due either to a high valence of the ion or to a high degree of adsorbability. Polyvalent cations give, therefore, irregular series when they are combined with monovalent anions. But monovalent *organic* cations act in the same way. For instance, strychnine nitrate, as well as new fuchsin, yields an irregular series with As_2S_3 sol, and AgNO_3 with the sol of HgS , because in each case the cation is strongly adsorbed," p. 85.

"In recent times, chemical arguments have been advanced which seem to indicate that the cellulose molecule is not exceedingly large. It has been erroneously assumed in organic chemistry that n , in the formula $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, is large; in reality, this quantity is completely unknown since we lack the means of determining the molecular size of a non-volatile and insoluble (i.e., non-molecularly dispersible) substance. From the researches of Bergmann and those of Pringsheim, one gains the impression that there is a possibility of obtaining cellulose temporarily—although only under unstable conditions—as a monomolecularly dispersed substance, in which case $n = 1$ according to the ebullioscopic method. These chemical investigations are thus a confirmation of the concept developed here, viz., that sols are polymolecularly dispersed particles. Other experiments of Bergmann prove that the development of the organic chemistry of proteins is proceeding in the same direction," p. 176.

"An important difference between suspensoids and emulsoids lies, as we have seen, in the fact that the latter, when deprived of their electric charge, do not flocculate. This is exactly the point which has led to a separation of the statics of emulsoids from that of suspensoids.

"In order to explain this difference, we must look elsewhere for a suitable hypothesis which can be tested experimentally. Evidently, emulsoids have a *second stability factor* which prevents the flocculation of the unchanged particles. Remembering that the condition of non-flocculation signifies a probability of adhesion not largely deviating from zero, we realise that this second factor, which keeps the colloiding particles from permanently uniting, must be of a different nature. Since the characteristic difference between suspensoids and emulsoids is due to the hydration of the particles, we immediately assume that it is the film of water which furnishes a second protective factor. In other words, emulsoid particles may be protected against flocculation both by their electric charge and by their hydration. When we have at our disposal a means of eliminating hydration, we can readily verify this assumption, p. 180.

"We have already seen that the addition of minute quantities of an electrolyte to a starch or an agar-agar sol removes the charge but not the stability. On adding alcohol to such a discharged sol, one observes an immediate flocculation. This proves, therefore, that we are dealing, in every case, with two stability factors but that it is immaterial in which order they are removed. The removal of one can be accomplished without evident effect, but the removal of both inevitably causes flocculation," p. 181.

"It has been shown that the power of salting out depends on both the nature of the cation and that of the anion. The different cations can be arranged in a series of decreasing precipitating power, from left to right, when used in equal molecular concentration. A similar series exists for anions. These series are called *lyotropic series*. Cation series: Li—Na—K—Rb—Cs and: Mg—Ca—Sr—Ba. Anion series: SO₄—Cl—Br—NO₃—I—CNS

"These lyotropic series are not only met when emulsoids are salted out but are also characteristic of a number of other physico-chemical phenomena. The effect of neutral salts on the rate of inversion of cane sugar and on other reaction velocities is determined by the order of the lyotropic ionic series. The same sequence is noticed in the displacement of the maximum density of water (at 4°); in the change in solubility of non-electrolytes, for instance, that of urea in water; and in the lowering of the surface tension of water. In the subsequent chapters we shall consider still other properties that are related to these lyotropic series," p. 183.

"We saw previously that the dehydration effected by alcohol results from the mass-law equilibrium between alcohol and water. Tannin, on the other hand, is a substance which lowers the surface tension considerably; in other words, it is strongly adsorbed. Hence, the large effect in small concentrations is presumably due to the adsorption of tannin by the colloidal particles.

"That this is really the case can be proved in the following manner: When another compound that is capable of exerting a displacing action is added to an agar-agar sol treated with tannin, the colloidal particles are freed, at least partly, from the adsorbed tannin; and, consequently, the emulsoid properties must return. Curiously enough, we can use, for instance, alcohol for this purpose. Investigation has shown that alcohol added in small amounts to an agar-agar sol, that has been dehydrated by tannin, increases the relative viscosity and brings back the property of gelatinizing, whereas the addition in quantities of about 50 per cent again prevents the setting of the sol as a result of the dehydration by alcohol," p. 186.

"Let us discuss, first of all, the viscosity of a gelatin solution as a function of the hydrogen-ion concentration. Loeb made an unusually extensive study of this relationship. It is to his credit that he paid particular attention to the hydrogen-ion concentration of the intermolecular liquid and did not confine his investigations to the concentration of the added acids and bases. In the course of his researches, he gradually dropped his early view that gelatin solutions were true electrolyte solutions; and the present writer is convinced that, had his untimely death not interrupted his work, he would before long have arrived at the theory

that is here propounded. His last experiments on the cataphoretic velocity of gelatin pointed clearly in this direction. Probably he would have been forced to retract erroneous statements regarding colloid chemistry made in previous years. As a matter of fact, he had already deserted his original viewpoints a number of times in the period from 1918 to 1923," p. 195.

"Briefly summarizing our ideas regarding the stability of suspensoids and emulsoids, we arrive at the following conclusion, which is best illustrated by means of four characteristic sols: (1) gold sol, (2) tin oxide sol, (3) agar-agar sol, (4) gelatin sol.

"The stability of these sols is dependent on the electric charge, on hydration, or on both. In the case of the first two sols there is practically no hydration; they are suspensoids, the stability of which is solely a function of their electric charge. The last two sols can exist on the strength of their considerable hydration alone, although they are generally stabilized by both charge and hydration.

"Between sol 1 and sol 2 there exists a difference already extensively discussed. The gold atoms in the periphery of the gold particle are not able to form a double layer of their own accord, but require an outside peptizing electrolyte in order to obtain a charge. The flocculation of such a sol is in perfect accordance with Freundlich's theory. The tin oxide sol, however, has a double layer, the inner coating of which is furnished by the sol itself. Since this inner coating may be positively or negatively charged, depending in the stabilizing electrolyte, two kinds of sol are possible.

"About the same difference exists between the two emulsoid sols mentioned above. The carbohydrate agar-agar is in itself little suited to the formation of a double layer. Traces of an electrolyte (possibly derived from the ash content) build up the double layer, and the phenomena of discharge are governed exclusively by the theory of Freundlich. The gelatin sol, on the other hand, possessing ionogen molecules, can form a double layer either in an acid or in an alkaline medium, thus greatly resembling the tin oxide sol.

"Hence, there is this difference between sols 1 and 2, and likewise between sols 3 and 4; viz., that sols 1 and 3 derive their double layers from absolutely extraneous constituents whereas in the second and the fourth cases one constituent of the double layer originates in the particle itself," p. 200.

"Loeb made numerous osmotic measurements, using the gelatin sol, and with the aid of a line of reasoning advanced by Procter and Wilson, he compared the results obtained with the data derived from an application of Donnan's theory. The agreement was obviously very good since his case was the one just mentioned. Loeb inferred, quite erroneously, that his system belonged to the type exemplified by Congo red, i.e., an electrolyte in true solution one ion of which—viz., the gelatin ion—cannot pass through the membrane. General objections to this view have already been developed. Here, too, we are justified in rejecting the conclusiveness of the arguments in the field of osmotic measurements for the simple reason that the agreement with Donnan theory holds just as well for a colloid in adsorption equilibrium with a peptizing electrolyte as it does for an electrolyte of the Congo red type," p. 207.

"Gelatinizing is the agglomeration of hydrated particles which retain the remaining water inside the capillary spaces between them. This agglomeration occurs, for sols of the type of aluminum oxide, simply by electrolyte-flocculation, and is, consequently, irreversible; whereas in cases of temperature-gelatinizing, the process takes place reversibly in some manner as yet unexplained," p. 217.

"Lyotropy is probably not a hydration pure and simple, but one that orients the dipoles of water. This explains at once, why, in the case of proteins, the lyotropic series are reversed when the charge of the protein changes from positive to negative. Here, too, the similar or dissimilar location of the hydrated water determines the order of the lyotropic phenomena." There is no reversal of the series with fibrin or gelatine.

On p. 245 the author says that water-in-oil emulsions are, as a rule, very viscous, or, to express it more correctly, plastic. This statement is true only for water-rich emulsions of this type.

Wilder D. Bancroft

The Chemical Coloring of Metals. By Samuel Field and S. R. Bonney. 21 × 14 cm; pp. xix + 264. New York: D. Van Nostrand Company, 1928. Price: \$4.00. The book is written avowedly for the craftsmen and the chemistry is, therefore, distinctly elementary. It gives a wealth of material to the chemist who may be interested in working out the theory of the processes. The quick methods of producing patines tend to give a transparent color like a wash. The patines produced in the course of centuries are usually more solid in color. This difference cannot be necessary and should not exist.

Incidentally, there are some puzzling chemical problems. Why should clean copper turn a rich rouge-brown color, p. 148, when boiled with a cupric chloride solution and why should sunlight give this a bluish shade, p. 134. Iridescent colors on zinc are obtained by heating with an alkaline copper tartrate solution, p. 205. "This is another of the blue organo-metallic compounds of copper. The solution is used at 110° F. and on zinc a succession of shades is produced, viz., coppery shade, yellow, light brown, crimson, blue, purple, pale purple, light green and finishing with light crimson. These shades are beautiful but not uniform. They give an iridescent effect. The cold solution works slowly, but is easily controlled. The warm solution works more rapidly, but is more difficult to control."

"It is about sixteen years since one of the authors was approached by a firm of telephone manufacturers to nickel-plate aluminum telephones. A refusal to undertake the work could not be taken as the order for the nickel-plated goods had been accepted, some of which were required for steamships and yachts. The nickel-plating was therefore undertaken on the understanding that not more than eighteen months' service could be expected or guaranteed. The work was done, and in less than this stipulated time the fittings had to be removed and were not replaced by similar work. Sea air has a most detrimental effect on aluminum. In the case of these fittings, the nickel-plate began to blister, especially where handled, and soon peeled.

"The at first apparent success of the plating brought forth many enquiries and other types of aluminum ware were tried. The writer has before him a candle-stick stem which was nickel-plated sixteen years ago. The plating is not perfect now, minor imperfections, consisting of pimples of the size of a pin-head, being obvious. The cost of the work was, however, prohibitive," p. 226.

Wilder D. Bancroft

Practical Physics. By T. G. Bedford. 22 × 14 cm; pp. x + 425 with 225 figures. London: Longmans, Green and Company. Price: 10 shillings, six pence. This text book of Laboratory Physics has been compiled from the manuscript notes in use in the author's classes at the Cavendish Laboratory, Cambridge, and takes shape as a result of long experience of laboratory practice. The standard attained is well in advance of intermediate work though not covering all the ground for the bachelor of science degree in Physics. The course would be admirably suited to students taking physics as subsidiary to an Honours Chemistry degree.

The book opens with a short introduction on the use and care of apparatus, methods of observation and recording of results. The part dealing with the experiments themselves is classed under the usual headings of mechanics and properties of Matter, Heat, Light, Sound, Magnetism and Electricity. The grouping of the experiments under these sections might perhaps be improved in one or two instances. For example, the optical lever should naturally appear with other instruments for measuring small distances instead of under the laws of reflection, but where a good index is provided this point is relatively unimportant.

An introduction to each experiment gives a short résumé of the theory concerned with it. Such brief deductions must necessarily begin with the phrase "it may be shown that . . ." and this point of departure is in every case suitably chosen; the deductions given being namely those connected directly with the practical side of the problem.

Descriptions of standard apparatus, such as spectroscopes, types of galvanometers, etc are confined to the general principles involved; the details of construction, which necessarily differ widely in different patterns, being left for explanation by the demonstrator. In

many cases however where special types of apparatus are described which could suitably be made in a laboratory workshop, the dimensions and construction are given fully. The section on Properties of Matter is particularly well dealt with in this way.

In some cases representative results of actual experiments are given though these are reduced to a minimum to avoid adding unduly to the size of the volume.

The practical experience behind the book is well shown in the full treatment given to the difficulties likely to be met with and the possible causes of failure of an experiment.

W. W. Barkas

Die elektrolytische Wasserüberführung und ihre Bedeutung für die Theorie der wässrigen Lösungen. By *Heinrich Remy*. Pp. 79. Berlin: Gebrüder Bornträger, 1927. Price: 5.60 marks. This monograph reviews in detail the two methods by which the transference of water during electrolysis has been estimated, viz:— (1) the Nernst method, depending on the introduction of a reference substance and developed on the experimental side notably by Washburn, and (2) the author's own method, involving the use of a diaphragm whereby in effect the middle point of the electrolytic column is mechanically fixed.

In connexion with the second method, which is discussed in greater detail than the first, it appears that, of the various diaphragm materials tested, parchment was by far the most satisfactory. The objection that the electrolytic transference of water would be masked by electro-endosmose is met by the proof that, however significant the latter phenomenon may be in very dilute solutions, it is negligible in electrolyte solutions of normal strength.

As will be readily understood, the two methods in question are both liable to considerable experimental error, and the results obtained for the electrolytic transport of water by one procedure only might be accepted with a certain reserve. The author, however, is able to record a notable agreement between the figures deduced by these very different methods, and there can be little doubt as to the approximate values of the net water transport in solutions of, say, the alkali chlorides.

For the purpose of calculating the absolute quantity of water associated with each ion—the water sheath or envelope—the author proceeds on the assumption that the anilinium and toluidinium ions are anhydrous. On this basis he finds that the envelope of the chlorine ion is approximately 3 molecules of water, and consequently the following values are assigned to the envelopes of the hydrogen and alkali metal ions: H⁺, 1.0; Li⁺, 12.6; Na⁺, 8.4; K⁺, 4.0. The relation of these results to the hydration theory and to modern views on electrolytic dissociation is briefly discussed.

J. C. Philip.

Katalyse mit kolloiden Metallen. By *Walter Hüchel*. 22 × 15 cm; pp. viii + 84. Leipzig: Akademische Verlagsgesellschaft, 1927. Price: 6 marks, unbound. The chapters are entitled: introduction; preparation of colloidal metallic catalysts; colloid catalysis; kinetics of catalysis with colloidal metals; mechanism of the catalytic hydrogenation by means of colloidal metals.

The title is much broader than the actual scope of the book which is limited explicitly to a discussion of laboratory methods, and practically to the work of Paal and of Skita, in other words to laboratory methods with colloidal metals of the platinum group. The real object of the book seems to be to advertize Skita.

The chapter on the mechanism of the catalytic hydrogenation by means of colloidal metals is obscure and unsatisfactory. The author considers that activation of hydrogen may be due: to monatomic hydrogen dissolved either as such or as an ion; to an unstable metallic hydride which decomposes, giving off atomic hydrogen; to an unstable metal oxide hydride; or to highly deformed hydrogen molecules. He does not like any of these hypotheses and is apparently sceptical of any activation of hydrogen being important. It therefore becomes necessary to consider the other constituent as activated and he adopts, apparently without proof, Skita's view that activation is due to the formation of a definite chemical compound between the metal catalyst and the unsaturated compound. No reference is made to the views of E. F. Armstrong, presumably because Armstrong did not work with metallic sols. This is a book of which anybody could be ashamed.

Wilder D. Bancroft

VARIATIONS IN THE SURFACE TENSIONS OF SOLUTIONS*

BY S. LAWRENCE BIGELOW AND E. ROGER WASHBURN**

Of all methods for measuring surface tension, the rise of liquids in capillary tubes is the simplest in application and in theory. But frequently it appears to be impossible to reproduce results with reasonable accuracy, while the cause of the trouble is not apparent. On this account the method seems to be falling into disfavor; which is unfortunate.

We undertook to discover, if possible, what some of these hidden difficulties might be and how to guard against them. We were successful in bringing to light some sources of error and in showing that they can be avoided by the application of simple precautions.

In this article we deal mainly with variations in the surface tensions of solutions with time.

Historical

A number of instances of such variations have been recorded in the literature. As early as 1869, A. Dupré,¹ while studying the surface tensions of aqueous solutions of soap, as shown by the vertical height to which fine jets of the solution rose under a definite pressure, conceived the idea that the surface tension of a freshly formed surface was greater than that of older surfaces.

Some twenty years later, Lord Rayleigh,² without previous knowledge of Dupré's work, reached the same conclusion. He measured the surface tensions of solutions of sodium oleate and of saponin, using the vibrating jet method for the freshly formed surfaces and the capillary rise method for the older surfaces. He showed that only in the older surfaces did the soap or saponin produce marked lowering. He believed this lowering to be due to the formation of an insoluble layer or "pellicle" of the organic material on the surface.

S. R. Milner,³ studied the phenomenon with sodium oleate solutions in greater detail. He observed that the fall in surface tension was most rapid at first, and then became slower until finally a constant value was reached. The more concentrated the solution the quicker it reached this constant value. Agitation reestablished the initial value and then the phenomenon repeated itself, but did not always result in the same minimum. He concluded that the decrease in surface tension is caused by adsorption of sodium oleate in the surface until a definite concentration is reached. This would occur quickly with concentrated solutions but might require hours when they were dilute.

* Contribution from the Chemical Laboratory of the University of Michigan.

**The work presented in this paper is taken from a dissertation presented by E. Roger Washburn in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

¹ A. Dupré: *Théorie mécanique de la Chaleur* (1869).

² *Proc. Roy. Soc.*, 47, 281 (1890).

³ *Phil. Mag.*, (6) 13, 96 (1907).

L. Berzeller,¹ observed a similar decrease in the surface tension of soap solutions with time.

P. Lecomte du Noüy² is the author of several papers and a book describing instances of surface tensions falling with time. He developed an instrument utilizing the method wherein the force is measured which is required to pull a wire ring off the surface of a liquid. He found, for example, that dog serum added to water or to a saline solution reduced the surface tension gradually. The maximum lowering was reached in from twenty to thirty minutes. Agitation produced an increase in the surface tension but not up to the original value. A second fall ensued but not to so low a value. Repetition gave variations between narrower and narrower limits until finally the surface activity of the serum (its ability to lower surface tension with time) seemed to be completely lost. This lessening of range of variations, this damping effect, must be due to some chemical reaction. Du Noüy says that all of the effects he observed may be due to one or more of the following causes; chemical change, adsorption in the surface, adsorption by colloids in the liquid, modification of molecular arrangement in the surface.

His results are most interesting, but the systems with which he works are complex and contain too many variables. We need careful studies with the simplest possible systems to establish fundamental principles before we can interpret such results as his with confidence.

He makes the following remarkable statement; "It is only through the ring method that it is possible to observe and study this phenomenon (changing surface tension) as it is the only procedure which permits the measurement of the surface tension of the same layer of liquid at very short intervals." This is manifestly in error. As has been said, S. R. Milner studied the change in surface tension by the capillary rise method which is obviously superior because the surface is not disturbed. Pulling off a ring and replacing it must seriously upset any molecular arrangement in the surface or any concentration gradient established by adsorption. It is indeed surprising that du Noüy succeeded in obtaining the results he did.

C. E. Davis, H. M. Salisbury and M. T. Harvey,³ using the drop weight method, observed a slight decrease in the surface tension of gelatin solutions with time. Here again it is surprising that the effect was observed, for during the formation of drops the surface is constantly agitated, and we and others have always observed that agitation tends to restore the initial values.

A study of the change of surface tension of solutions of gelatin, casein, albumin and haemoglobin has been made by J. M. Joblin⁴ applying both the drop weight and the capillary rise methods. He found that the longer the time he allowed for each drop to form, the greater the observed change in surface tension. This is quite as it should be, and is convincing evidence that the method is unsuited for anything but qualitative purposes.

¹ *Internat. Z. physik. Chem. Biol.* 1, 124 (1914).

² *J. Exp. Med.*, 35, 575, 707; 36, 113 (1922); *Science*, 59, 580, 1539; "Surface Equilibria of Biological and Organic Colloids" (1926).

³ *J. Ind. Eng. Chem.*, 16, 161 (1924).

⁴ *J. Phys. Chem.*, 29, 270, 897, 1129 (1925).

His results with the capillary rise method were somewhat irregular, especially when wide capillaries were used. Frequent "throbbing" of the meniscus he ascribed to molecular rearrangements in the surface. He observed that often a period of inactivity intervened before the fall began. This lasted but a few seconds with moderately concentrated solutions but grew longer as the dilution was increased. We shall refer to this again in the description of our own work.

It is obvious from this brief review that the phenomenon is of especial interest to physiologists, and with good reason, as it doubtless plays important roles in life processes. Substances such as gelatin, albumin, serum and the like are too indefinite and solutions containing more than one solute are too complex to serve for the establishment of the underlying principles on a satisfactorily convincing basis. A study of the phenomenon as shown by the simple solutions of well-defined chemical compounds is needed, and this we hope we have, in a measure, supplied.

Apparatus and Methods

We adopted as our model the apparatus and methods so ably developed and described by T. W. Richards¹ and his co-workers and endeavored to maintain their standards of accuracy in our work.

We employed the customary methods and had the customary difficulty in selecting a few short lengths of capillary tubing of satisfactorily uniform bore. The range, which careful calibration proved to be uniform in bore, was included between two rings etched in the glass. These tubes were fashioned into capillarimeters of the type shown in Figs. 1, 2, 3, and 4.

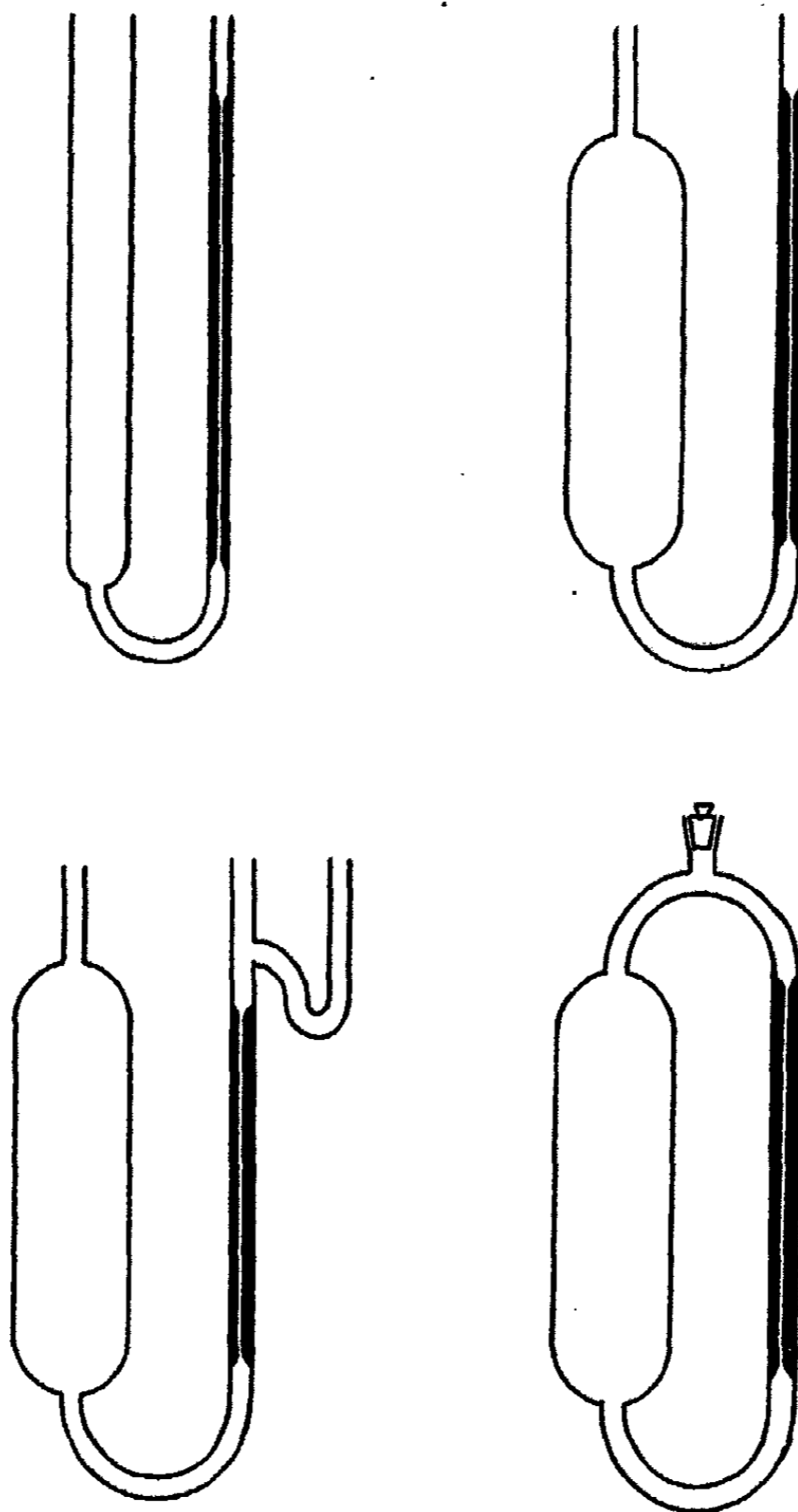
In type 1 the wider reference tube is not so wide that the capillary ascension in it can be neglected. The correction is easily applied in most cases, but with constantly changing surface tensions it introduces an inconvenient complication. Therefore we used these only for preliminary work. All of our final measurements were made with capillarimeters of types 2, 3, and 4, the reference tubes of which were at least 38 mm. in diameter. Richards has found that in a tube of this diameter, the central portion of a water meniscus is essentially a flat surface.

The capillarimeters were used in a thermostat which was fitted with plate glass windows front and back. An opaque shield placed between the capillarimeter and the electric light in the rear and just below the level of the large meniscus, as recommended by Richards, aided materially in giving sharply defined images. The cathetometer was graduated to read to 0.05 mm. Its telescope was equipped with a 72 mm. microscope objective, which gave a clear cut, magnified view of the meniscus.

Following the usual precaution, the meniscus was raised and lowered several times and then allowed to fall to its equilibrium position before a first reading was taken. This raising and lowering was produced by blowing or drawing

¹ J. Amer. Chem. Soc., 37, 1670 (1915); 43, 834 (1921).

through a train of calcium chloride, soda lime and cotton connected to the wide arm of the capillarimeter so there was no chance of contaminating the capillary meniscus.



FIGS. 1-4

We designated our capillaries by letters and determined their radii by the usual method of measuring the lengths and weights of threads of mercury, too well known to require description. We also determined their radii by observing the capillary rise of water and substituting in the equation $rh = a^2$, where r is the radius sought, h the true or corrected height to which water rises and a^2 is its capillary constant. Richards and Carver¹ obtained for this constant, at 20° the value 14.877 which we used.

¹ J. Am. Chem. Soc., 43, 834 (1921).

Our results by the two methods checked satisfactorily. For example, we found the radius of capillary C by the mercury thread method to be 0.0169 cm.; by the surface tension method we found 0.0166 as a minimum and 0.0167 cm. as a maximum. The radius of capillary 1P we found by the mercury thread method to be 0.0210 cm. (minimum) 0.0211 cm. (maximum); by the surface tension method we found 0.0211 cm. (minimum) and 0.0212 cm. (maximum). Agreement being so close we felt the surface tension method was sufficiently reliable and preferred it because of the accurate temperature control in the thermostat and because it is so much more easily and rapidly carried out.

The cleaning of the tubes is important. We tried the usual cleaning agents such as aqua regia and chromic acid but finally concluded that the most consistently good results could be obtained by the following procedure. Hot alkaline permanganate solution is drawn through the tube for several minutes, followed by hot hydrochloric acid to dissolve any manganese dioxide formed. Hot water is then drawn through the tube for fifteen or twenty minutes. The tube is dried in an electric oven, the last traces of moisture being removed by drawing dry, filtered, air through the hot tube.

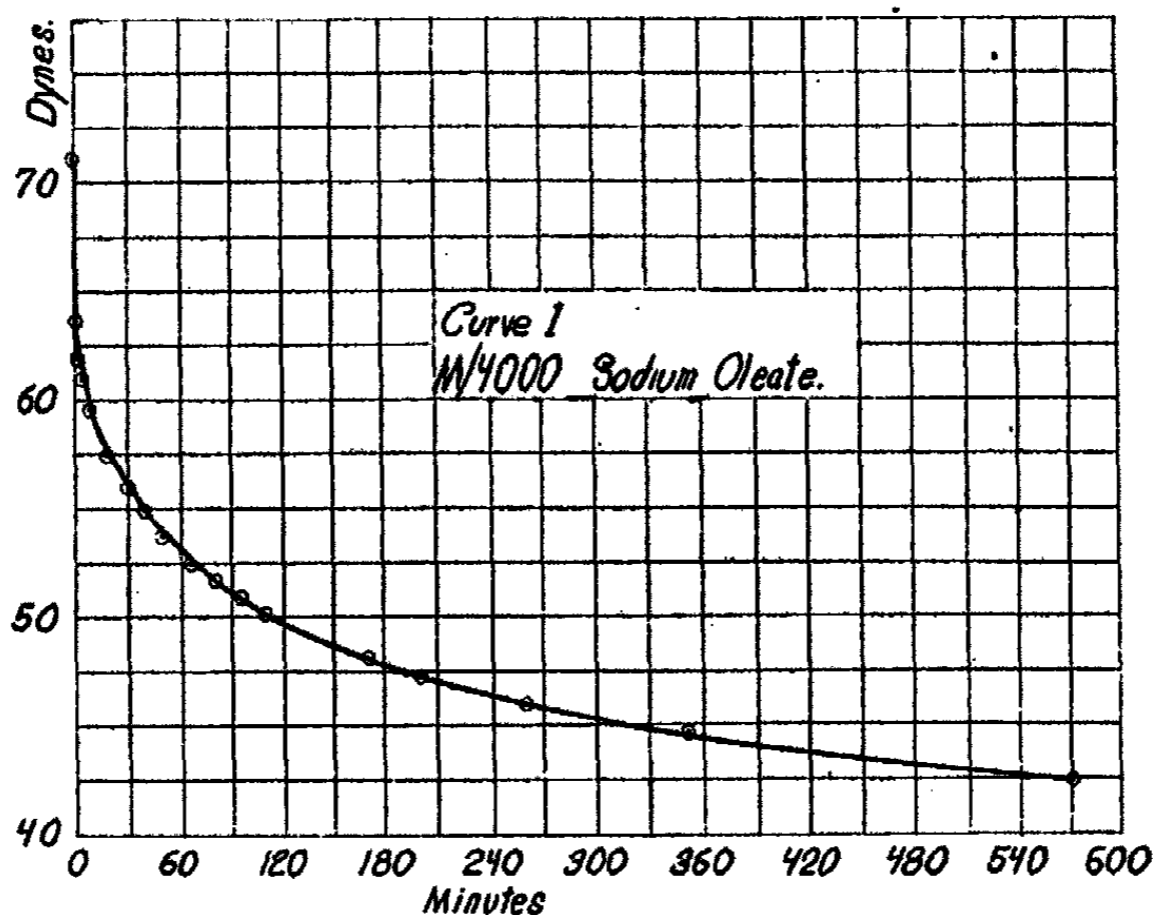
Whether or not a tube is clean can be determined by the behavior of the meniscus before starting an experiment. The meniscus is blown up, through the train already described, and then falls evenly with no indication of sticking, to its equilibrium point. The walls drain apparently dry and no visible droplets remain. It is drawn down and allowed to rise to its equilibrium point. This must coincide exactly with that obtained after falling. The motion must be perfectly smooth and there must not be the slightest flattening or other distortion of the meniscus when in motion. If these conditions are fulfilled the tube is adequately clean.

Making ready for an experiment we poured into the wide arm of the capillarimeter enough of the solution to cause the meniscus in the capillary to stand at some point between the etched lines which marked the uniform section of the tube, and then fastened it vertically in the water of the thermostat. By blowing and suction the meniscus was caused to rise and fall and its behavior studied critically. After enough time had elapsed for the temperature of the apparatus to reach that of the bath, the solution was vigorously agitated and the first reading was made of the meniscus in the capillary and immediately thereafter of the level in the reference arm. Other readings were taken as often as seemed necessary to follow the changes being observed. The meniscus was not agitated after the first reading was made unless so stated in the reports of the results.

In order to abbreviate our report and to facilitate comparisons of results obtained with different tubes, we have omitted the cathetometer readings and capillary heights, but have calculated the corresponding surface tensions in each case according to the formula, $\gamma = \frac{1}{2}ghr(D - d)$, wherein γ is the surface tension, g , the gravitational constant, h , the corrected rise, r , the radius of the tube, and $(D - d)$, the difference between the densities of the liquid and vapor phases. With dilute aqueous solutions this value is almost

exactly the difference between the density of water and that of air saturated with water vapor. And so we used this value; the error thus introduced is negligible as will be shown later.

Solutions of Sodium Oleate. All of our solutions were made up by weight. The sodium oleate was obtained from Mallinckrodt. It was not further purified by us, but was dried at 90° to constant weight. The greater part of

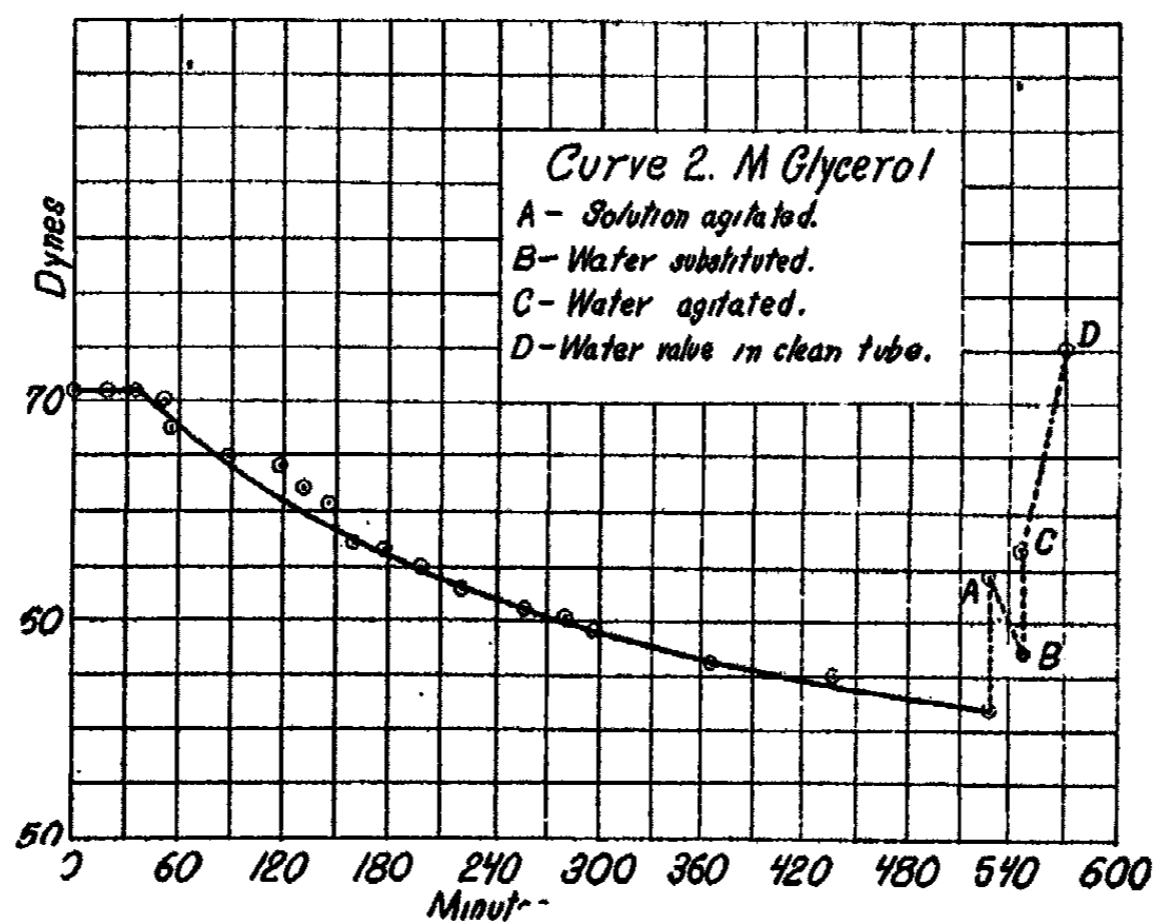


the work which we carried out with this substance was completed in 1924, before the publication of the experiments by J. M. Johlin (*loc. cit.*). The results which we obtained agree essentially with his, especially as to maximum and minimum values, and we experienced the same difficulty in reproducing exactly any particular experiment carried out with very dilute solutions. The rate of fall which we observed was somewhat slower than that observed by Johlin, though the difference is not great considering the difficulty of working with dilute solutions of this material in fine capillary tubes. Following are the details and results of one of these experiments selected as typical of the many which we did.

| Time elapsed | Surface tension | Time elapsed | Surface tension |
|--------------|-----------------|--------------|-----------------|
| 0 | 71.0 dynes | 65 minutes | 52.5 dynes |
| 1 minute | 63.7 " | 80 " | 51.7 " |
| 3 minutes | 61.9 " | 95 " | 50.8 " |
| 5 " | 61.0 " | 110 " | 50.2 " |
| 10 " | 59.6 " | 170 " | 48.2 " |
| 20 " | 57.5 " | 200 " | 47.3 " |
| 30 " | 56.0 " | 260 " | 46.0 " |
| 40 " | 54.9 " | 350 " | 44.7 " |
| 50 " | 53.7 " | 570 " | 42.4 " |

These results are plotted as Curve 1.

Solutions of Glycerol. The glycerol was purified by repeated fractional distillation under reduced pressure; the fraction which we used distilled at 200° (uncorrected) under 35 mm. pressure. It is particularly difficult to reproduce an experiment with solutions of glycerol. The reasons for this we do not surely know but we shall offer a possible explanation of the apparently erratic behavior after presenting the experimental data.



| Time elapsed | Surface tension | Time elapsed | Surface tension |
|--------------|-----------------|--------------|-----------------|
| 0 | 70.7 dynes | 179 minutes | 63.5 dynes |
| 19 minutes | 70.7 " | 199 " | 62.7 " |
| 34 " | 70.7 " | 221 " | 61.7 " |
| 49 " | 70.3 " | 231 " | 61.2 " |
| 54 " | 69.0 " | 258 " | 60.8 " |
| 87 " | 67.8 " | 283 " | 60.4 " |
| 119 " | 67.4 " | 298 " | 59.8 " |
| 130 " | 66.3 " | 368 " | 58.3 " |
| 143 " | 65.5 " | 438 " | 57.7 " |
| 159 " | 63.8 " | 528 " | 56.0 " |

These results are plotted as Curve 2.

After the last reading the solution in the capillarimeter was agitated by drawing it down and blowing it up in the capillary. This caused the surface tension to rise to 62.2 dynes, (point A on the curve). The solution was then carefully withdrawn from the instrument and replaced by an equal amount of water. Under these circumstances the water showed a surface tension of only 58.5 dynes, (point B on the curve), not much different from that of the solution of glycerol which it replaced. Vigorous agitation increased the value,

but only to 63.4 dynes, (point C). The capillarimeter was then carefully cleaned and dried. After this, water in the capillarimeter gave its proper surface tension, 72.6 dynes, as shown by point D on the curve.

This behavior would lead one to believe that during the first part of the experiment glycerol was adsorbed on the glass walls of the capillary and was not all removed, either by agitation or by the removal of the solution.

Another experiment of the same type showed, in addition, the following interesting fact. After the solution had stood in the capillarimeter overnight, during which the surface tension fell from 70.6 dynes to 56.9 dynes, the solution was removed and water was substituted. When the amount of water in the capillarimeter was such that the meniscus stood in a part of the tube below that point at which the solution of glycerol meniscus had stood, the surface tension observed was 56.8 dynes. When more water was added, so that the meniscus came to rest at a point above that at which the solution meniscus had stood, the value observed for the surface tension was 72.2 dynes, very nearly the value to be expected for pure water. Since the water was added through the wide arm of the capillarimeter the surface of the meniscus was not changed by the addition, the meniscus was simply raised to a higher level. This tends to confirm the idea that glycerol is adsorbed on the glass walls in that portion of the tube in contact with the solution and is only removed with difficulty by agitation or by washing with water.

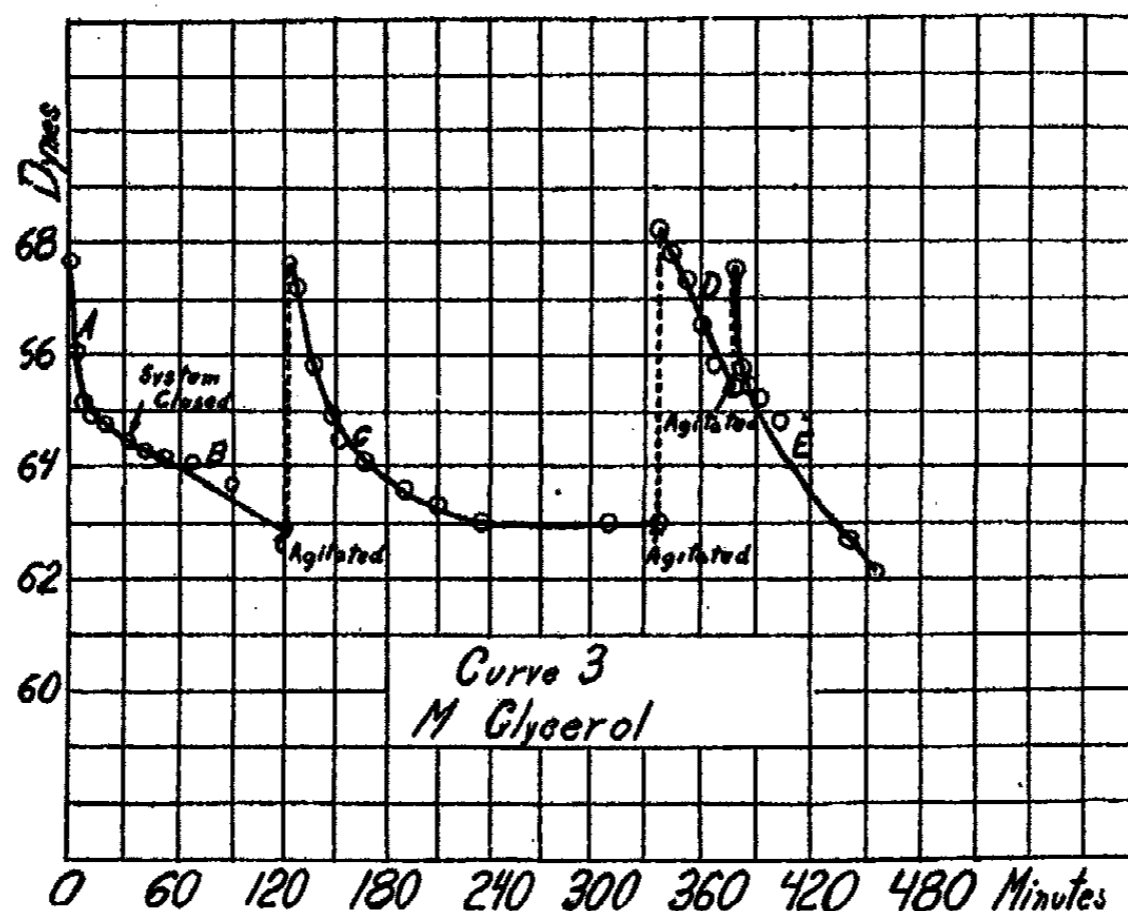
At least three later experiments confirmed these results as far as rate of fall is concerned. The time elapsing before the fall started and the effect of agitation, however, were not always the same. Several experiments with solutions of glycerol of the same concentration as that used above, have failed to show any change in more than an hour. In such cases, when the fall did start, the rate with which it progressed was often very much more rapid than that shown in Curve 2. Sometimes when the fall had failed to start for an unusually long time it was caused to start by a gentle agitation. These facts lead one to believe that the phenomenon which is responsible for the fall had been proceeding during the period of inactivity, but that the meniscus for some reason or other was prevented from responding. Something in the nature of a metastable state developed. In these experiments we had every reason to believe that the capillary was clean, but the fact that no change took place could be interpreted as indicating that the tube was not entirely free from foreign matter.

Evaporation of Water. It seemed that the decrease in surface tension might possibly be due to evaporation of water from the meniscus, leaving a more concentrated solution of glycerol, with a resulting lower surface tension. Vigorous agitation should correct this condition, giving a higher surface tension.

In order to determine whether or not this is a probable explanation of the phenomenon we carried out experiments in a type of capillarimeter which could be opened or closed at will, (Fig. 4). When the capillarimeter is closed the atmosphere within it should become saturated with water vapor, there should be no more evaporation and no fall, from this cause at least.

These experiments were carried out at 40° instead of 20° in order that the atmosphere should become saturated with water vapor in less time. The results of such an experiment are shown in Curve 3.*

These results are not in accord with what we should expect if our observed variation were due to the evaporation of water. Closing the system would stop the fall of the meniscus, if the vapor phase is saturated with water vapor,



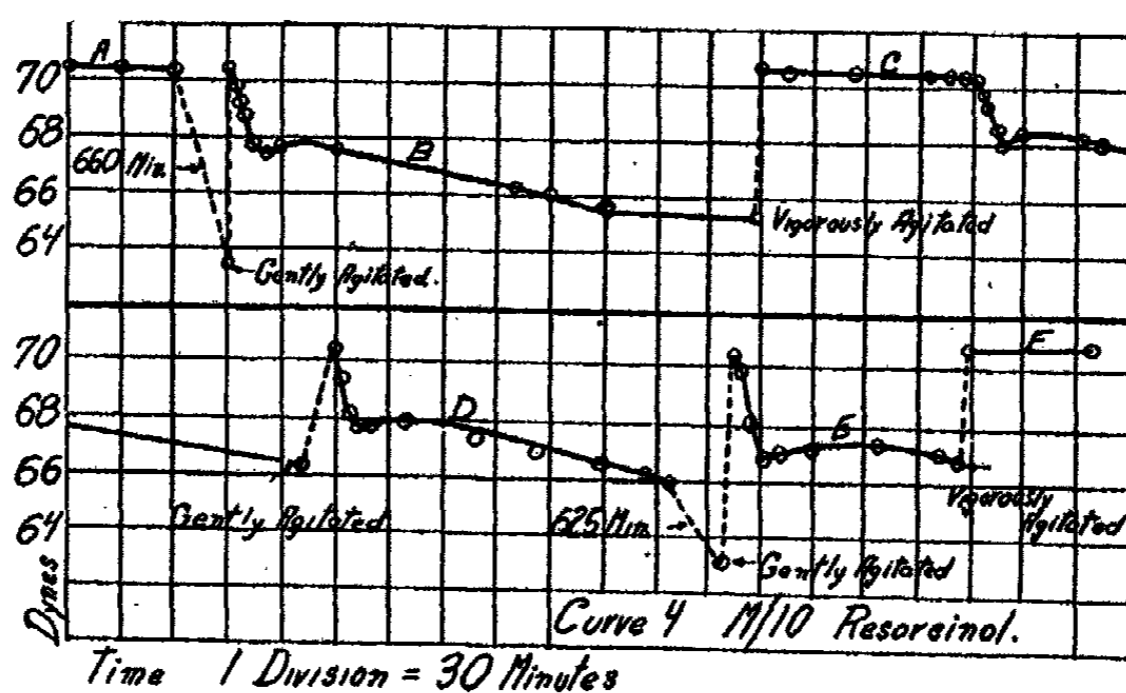
but it does not. After agitation of the solution in the closed capillarmeter by tilting it to and fro and the consequent restoration of the meniscus to its original condition, the small gaseous volume is surely saturated and there should be no fall at all. But falls occur repeatedly as shown. Not only this, but the fall denoted by part E of the curve is more rapid than that denoted by A, although during A the capillarmeter was open to the air, while, when E was started the instrument had been closed for five hours and forty-six minutes and the vapor phase was surely saturated.

On the other hand the results are in accord with what we would expect if the fall is due to an increased concentration of the glycerol at the interface between the solution and the glass walls, as well as at the solution-vapor interface.

Experiments such as resulted in Curve 2 indicate that if sufficient time be allowed some glycerol will become so firmly adsorbed on the glass walls that even vigorous agitation of the solution does not remove it. The agitation, by tilting, which we used in our closed system experiments, is of necessity comparatively gentle and quite inadequate to remove the adsorbed glycerol;

* We have drawn our curves to scale with care and believe we have included in them all information of interest to a reader. Therefore, we omit the extensive tabulations from which they were constructed.

even when pure water is substituted for the solution the low surface tension persists, presumably due to this adsorbed layer. However, if time has not been allowed for this firm adsorption of glycerol a gentle agitation will bring about uniformity in the concentration of the solution in the capillary. The original high surface tension, characteristic of the homogeneous solution against a clean glass surface, will then be observed. The time required for the glycerol to become thoroughly attached to the walls seems to vary, in the neighborhood of twelve hours being required when working at 20°, and a longer time when working at 40°.



Solutions of Resorcinol. The resorcinol which we used was Mallinckrodt's U.S.P. grade. Solutions of this material show a decreasing surface tension with time. In the results of the typical experiment which we give below we desire to call attention to the effect which the degree of violence of the agitation has upon the nature of the surface tension change which follows it.

The violence of the agitation which causes the surface tension to return to its maximum value after a fall has taken place, has a pronounced effect on the length of time which will elapse before the fall will start again. Part A of Curve 4 shows that the surface tension was constant for more than an hour after the solution was poured in the capillarimeter. A decided drop took place, however, during the next eleven hours. A gentle agitation then caused the surface tension to return to its maximum value. Part B shows that the drop started at once after this gentle agitation. After reaching a low value the solution was vigorously agitated, resulting again the maximum value. The two hour period which elapsed, after this more violent agitation, before the fall started is shown in part C. The effects of two more gentle agitations and a second violent agitation are shown in parts D, E, and F.

Periods of inactivity of this sort have been noticed by us in work with solutions of other organic substances. J. M. Johlin observed similar periods of inactivity with dilute solutions of sodium oleate and casein, but makes no

attempt to explain them. We recognize that our suggestion that a metastable state is established is inadequate as an explanation, but feel that it contains a hint worth following.

The suggestions we made in connection with our experiments with solutions of glycerol, are at least plausible here also. Let us assume that the lower surface tension values are due to the adsorption of the solute on the glass walls of the capillary and at the liquid-vapor interface of the meniscus. The gentle agitation serves to remix the solution in the meniscus but does not remove the adsorbed layer from the walls. The solution, now uniform, shows its appropriate surface tension, but adsorption in the meniscus starts at once and the surface tension soon falls. A vigorous agitation, on the other hand, not only remixes the solution in the meniscus but also removes the adsorbed layer from the walls. The fall is delayed by this treatment; perhaps a layer of the solute has to be adsorbed on the walls before the increase in concentration in the surface layer of the meniscus starts, or becomes effective in lowering the surface tension.

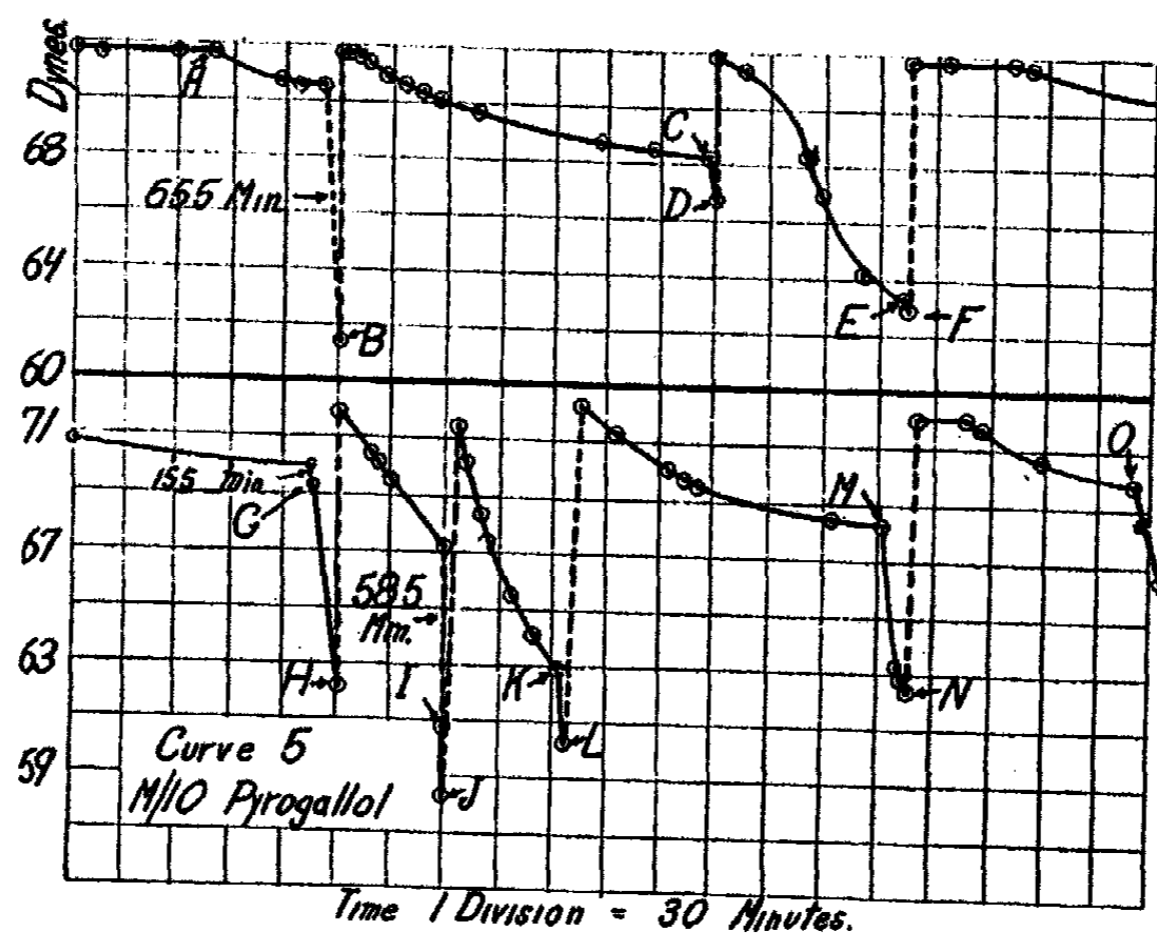
We observed a rather curious and interesting phenomenon with these solutions not shown in the curves. If, when the surface tension is at a minimum value, the meniscus is drawn down still farther in the capillary and then is allowed to ascend of its own accord, it rapidly comes back to the point at which it stood before it was lowered. No matter how far it is lowered, or how many times, the meniscus flies back to its original position as though drawn by a rubber band. If, however, the meniscus is gently forced a few millimeters above, not necessarily to its maximum point, and then lowered, it will fly up to the point to which it was forced. It does not hesitate as it passes its old minimum value. If the meniscus is forced above its maximum, or original value, it will fall to this point; if it is then drawn below it will rise to the same point.

A plausible explanation for this behavior is as follows. Water evaporating from the walls left wet by the descending column leaves a thin invisible layer of the solute. When the meniscus is drawn down and is allowed to fly back it will stop when it reaches the thin layer of the solute, because if it went further, it would dissolve the solute, become more concentrated and have a lower surface tension. When the meniscus is forced up a short distance it dissolves the solute from the walls and then will, if lowered, come back to the new and higher level where the walls are still coated with the comparatively dry solute.

Another of the puzzling phenomena which we noted in these experiments with resorcinol is the fact that a slight rise often takes place after a rather rapid fall. The rise, never amounting to more than a fraction of a dyne, is not always the same, nor does it always occur at the same point of the curve. After this rise has taken place the surface tension proceeds to fall slowly to some point below that at which it started to rise. Irregular results similar to these were noted by J. M. Johlin in work with solutions of gelatin. In the light of recent work of du Noüy, one may be justified in ascribing this slight rise, followed by a fall slower than the initial fall, to some sort of molecular orienta-

tion or rearrangement taking place in the surface layer. There is, however, no experimental proof that such an orientation would result in such a rise. We cannot ignore, on the other hand, a peculiar phenomenon which happens as consistently as this one has happened.

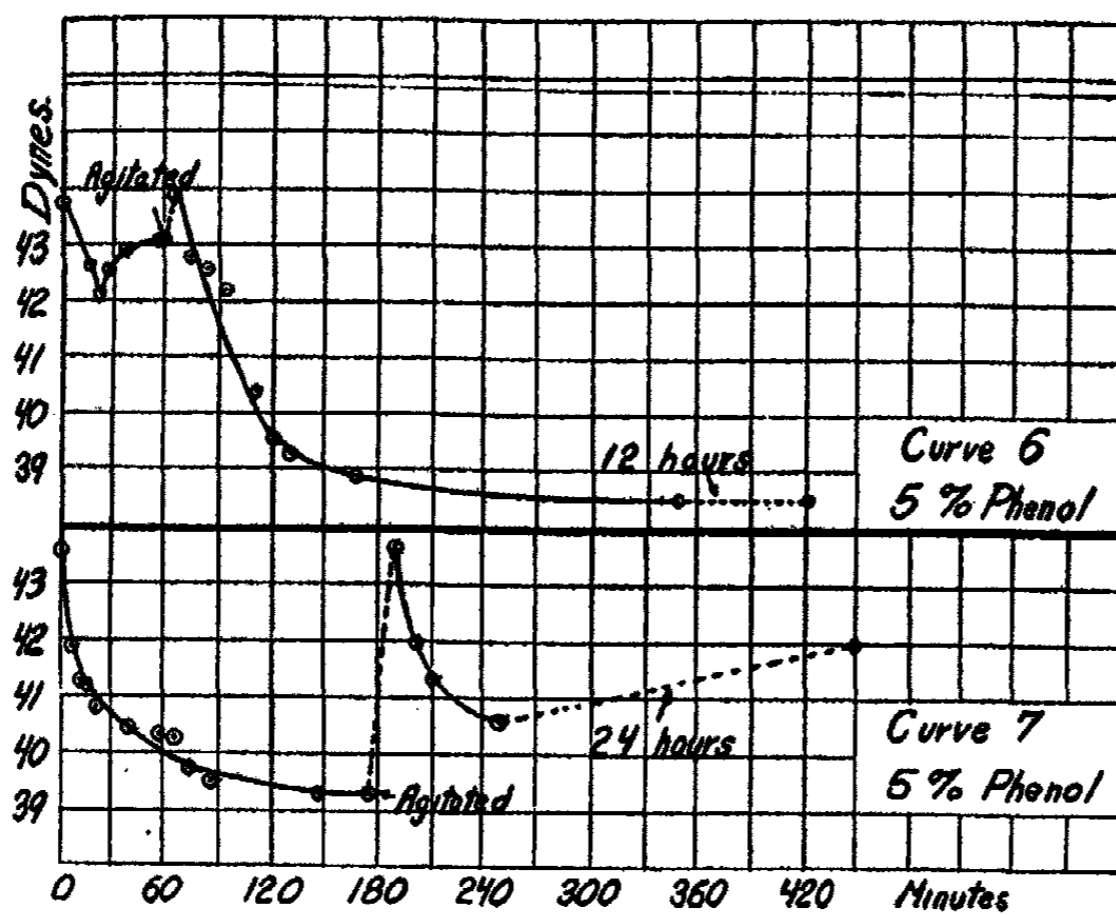
Solutions of Pyrogallol. The pyrogallol which we used was a standard C.P. grade.



At A and B vigorously agitated throughout the capillary. At C slightly agitated below the resting point. At D slightly agitated throughout the capillary. At E slightly agitated below the resting point. At F vigorously agitated throughout the capillary. At G vigorously agitated below the resting point. At H slightly agitated throughout the capillary. At I vigorously agitated below the resting point. At J slightly agitated throughout the capillary. At K vigorously agitated below the resting point. At L vigorously agitated throughout the capillary. At M vigorously agitated below the resting point. At N vigorously agitated throughout the capillary. At O slightly agitated below the resting point.

These results are of the same nature as those which we obtained with solutions of resorcinol and are readily explained by the same reasoning. A vigorous agitation throughout the tube is often followed by a period of inactivity before the fall starts. This is shown by the portions of the curve following the points B, F, and N. The duration of this period is not always the same, in fact, the fall sometimes starts almost at once but proceeds slowly as is shown by the curves following the points A and L. One reason for this difference undoubtedly lies in the fact that the agitation is not always of the same degree of violence; it is also probable that the adsorption on the walls has progressed to a greater extent in some cases than in others. According to our hypothesis

the vigorous agitation not only remixes the solution in the capillary but also removes the adsorbed layer from the walls. A gentle agitation, however, serves only to mix the liquid in the surface layer with the rest of the solution, and does not remove the layer from the walls. Such gentle agitation is invariably followed by a comparatively rapid fall as is shown by the steep portions of the curve following D, H, and J.

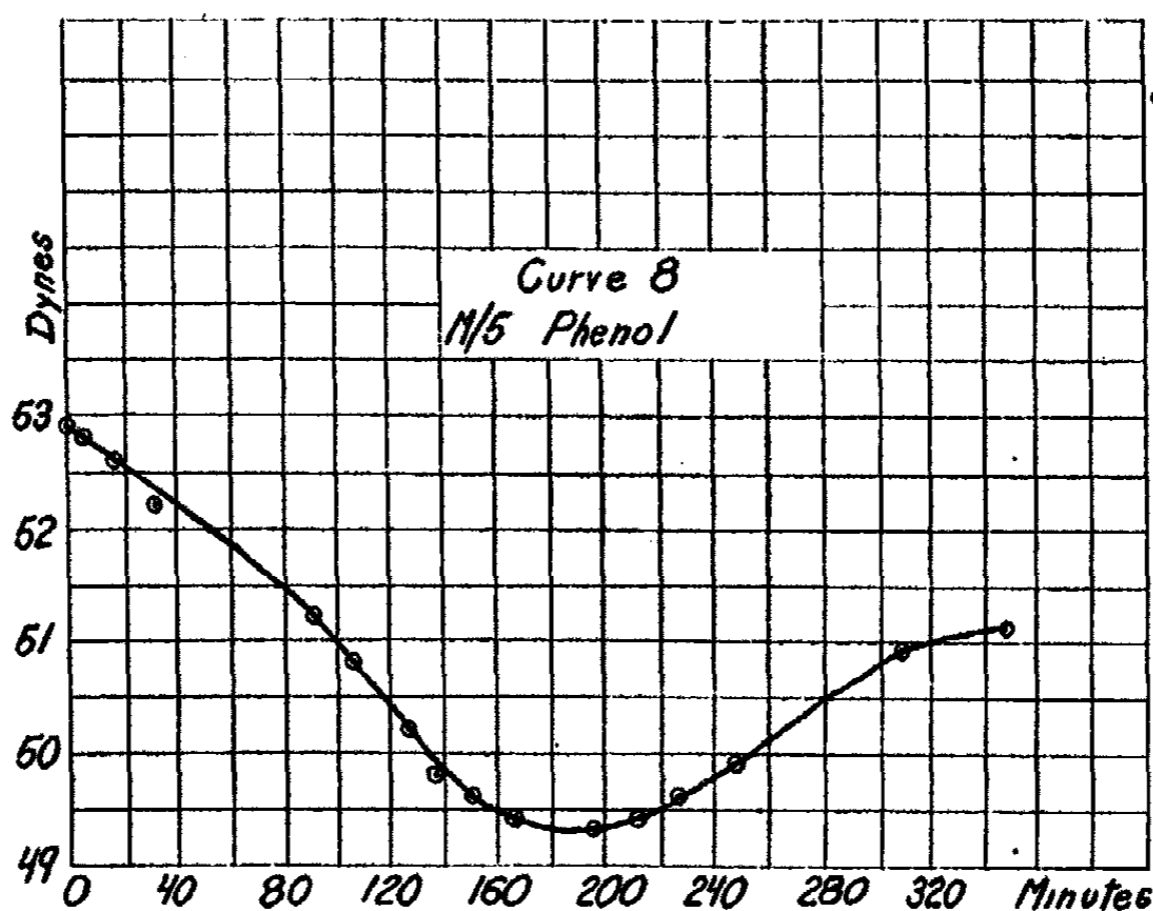


The fact that agitation, either gentle or vigorous, below the resting point of the meniscus in each case caused the liquid to come to rest at a point lower than that at which it had stood before is evident, (see points C, E, G, I, K, M, and O). This indicates that here has been lag in the fall, the decrease had not been quite keeping up with the adsorption of the solute. The agitation upset a metastable state and then the system moved to the proper point, as determined by the amount of adsorption which had taken place.

These experiments, showing the effect of agitation on the surface tension changes of solutions of glycerol, resorcinol, and pyrogallol, are, we feel, of significance. They are the most direct experimental evidence which has yet been offered in support of the theory that falling surface tensions can be caused by the adsorption of the organic solute at the liquid-glass interface as well as the liquid-vapor interface.

Solutions of Phenol. Variations in surface tension which are not readily accounted for on the basis of the theory which we have just outlined have been observed to take place with solutions of phenol. Many experiments were carried out with this substance in a vain attempt to reproduce conditions so that the same type of variation could be consistently obtained. The following curves illustrate the kind of irregularities which occur.

The fall in surface tension usually started at once, either with a new solution or with a freshly agitated one, although there was sometimes a short period of inactivity. The initial maximum values were reproducible without difficulty. In most of the experiments it was noted that, after a fall had taken place, the meniscus would slowly rise again to some point midway between the minimum and maximum values. This reversal would sometimes occur



within an hour after the start of an experiment, while in other cases several hours would pass without interruption of the steady downward trend. This rise is probably caused by the same phenomenon as that which was involved in experiments with resorcinol, and is perhaps of the same nature as that which caused the irregular results noted by J. M. Johlin with solutions of gelatin, and du Notty with solutions of sodium oleate. At present we cannot account for this rise, and are unable to regulate the conditions which determine it.

Solutions of Other Substances. Surface tensions decreasing with time have also been noted and studied with solutions of oxalic, propionic, and succinic acids. As these studies discovered nothing beyond what we have described, details are omitted. Some other substances, which from analogy one would expect to form solutions showing decreasing surface tensions with time, as acetic acid, or sodium acetate, have very little effect on the surface tension of water.

Solutions showing an Increasing Surface Tension with Time

In preparing capillarmeters for experiments, after the cleaning and washing, they were dried by drawing dry air through them. In the preliminary stages of our work we employed an ordinary drying train, containing calcium chloride, soda lime, and cotton, and after passing through this, the air passed

through a rubber tube before entering the capillarimeter. We became suspicious of this tube and felt that it was at least possible that minute solid particles, or gaseous emanations from the rubber, might contaminate the walls of our instrument. In order to determine what effects such contaminations might have, we attached a rubber tube which had been in use for some time on a Bunsen burner. This was exceedingly effective and surface tension values obtained after this treatment were most erratic. We substituted glass tubes and ground-glass joints in such a manner that the air came in contact with no rubber before entering the instrument, thus effectually eliminating trouble from this source.

But evidently something from the rubber was one of the hitherto overlooked sources of error for which we were searching. We decided to investigate this. Accordingly we passed illuminating gas through a clean capillarimeter for two or three minutes, washed the capillarimeter twice with water, and then determined the surface tension of water. We were surprised to observe an increase with the passage of time. In one hundred and fifteen minutes the surface tension increased from 70.7 dynes to 72.2 dynes.

Illuminating gas is of indefinite composition, accordingly we turned to pure gases. We passed hydrogen, nitrogen, oxygen, carbon dioxide, sulfur dioxide, and methane through clean capillarimeters, determining the surface tension of water in them after each treatment. The values obtained differed but little from the surface tension of pure water. In no case could we detect an indication of an increase in surface tension with the passage of time.

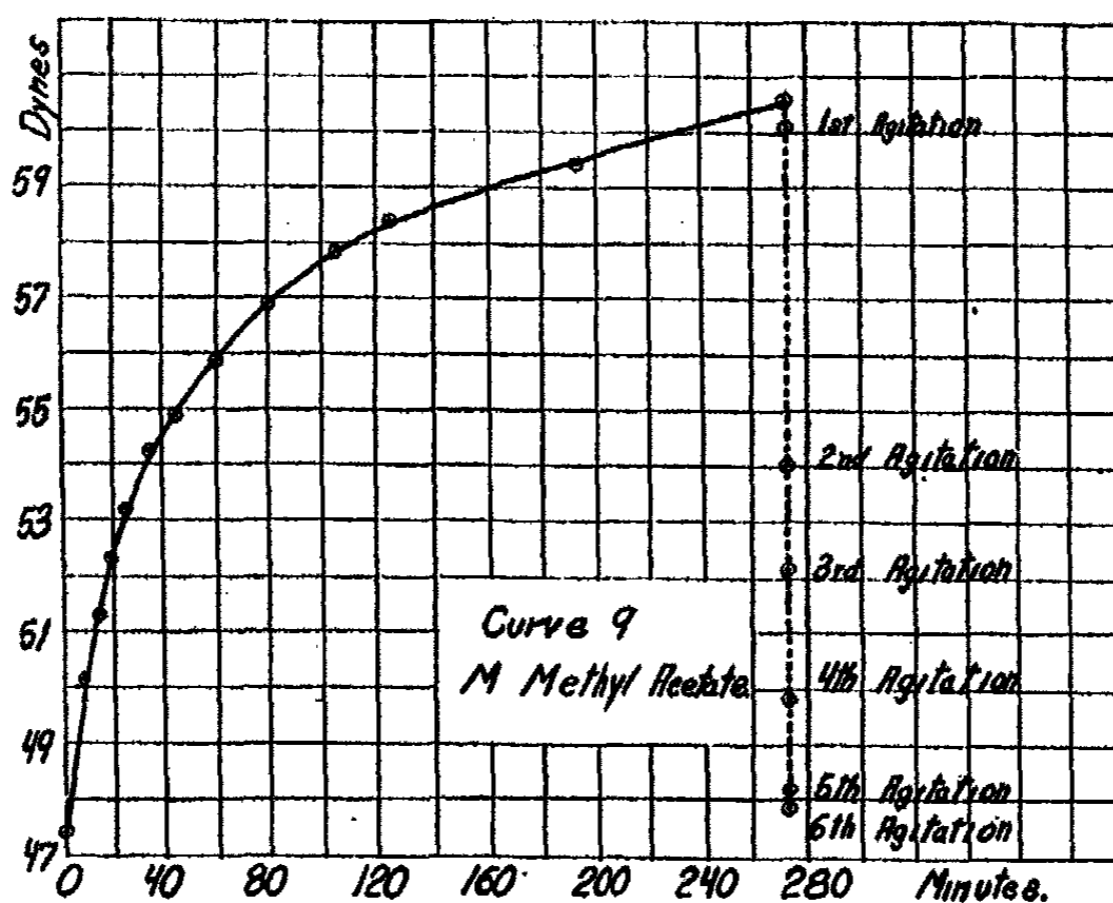
But these gases by no means exhaust the list of substances present in illuminating gas. Something from the gas must have clung to the walls. It might act in either of two ways. First, soiling the walls it would cause us to get too low a result, then, dissolving in the water the walls would become clean, and we should get the higher, correct value. Or, second, this foreign material might dissolve in the water at once and produce a lowering of its surface tension, and then it might evaporate from the meniscus until pure water was left, with its corresponding value.

Solutions of Amyl Acetate. Following this idea we turned to volatile substances which might be expected to evaporate from the surface of a water solution. Naturally we selected definite chemical compounds. Our first qualitative experiments were made with solutions of amyl acetate. We added one drop of amyl acetate to 100 cc. of water and put the solution in a capillarimeter, and were gratified to observe an increase in surface tension from 62.6 dynes to 69.6 dynes in half an hour. In observing the changing surface tension we were guided by our previous experience with falling surface tensions and so refrained from agitating the solution before each reading; we merely watched it climb.

This decided increase led us to study in a semi-quantitative manner the solutions of several different substances of the same type. The organic liquids used were purchased from Eastman Kodak Co., and unless so stated were

not purified further by us. Conductivity water was used in making up the solutions. These studies were only preliminary in nature, and the results should be considered as relative only.

Solutions of ethyl acetate, propyl butyrate, and butyl acetate show the phenomenon. A small increase in surface tension with time was noted with a dilute solution (about 2%) of ethyl alcohol. Aqueous solutions of amyl alco-



hol, propyl alcohol, and iso-propyl alcohol, displayed more pronounced increases with time. Ethylene dichloride and acetone when dissolved in water also gave definite increases in surface tension as time elapsed.

In general, the greater the initial lowering of surface tension caused by the solute the greater and more rapid is the increase following. With the substances we used, the higher the molecular weights the greater the effects on the surface tension of water. The solubility in water, however, decreases with increasing molecular weight and this fact limits the number of substances which we can use advantageously.

Solutions of Propyl Formate. A fifth molar solution of propyl formate showed an increase in surface tension from 47.8 dynes to 62.8 dynes in two hours. Agitation caused the surface tension to return to its minimum value from which a second increase took place.

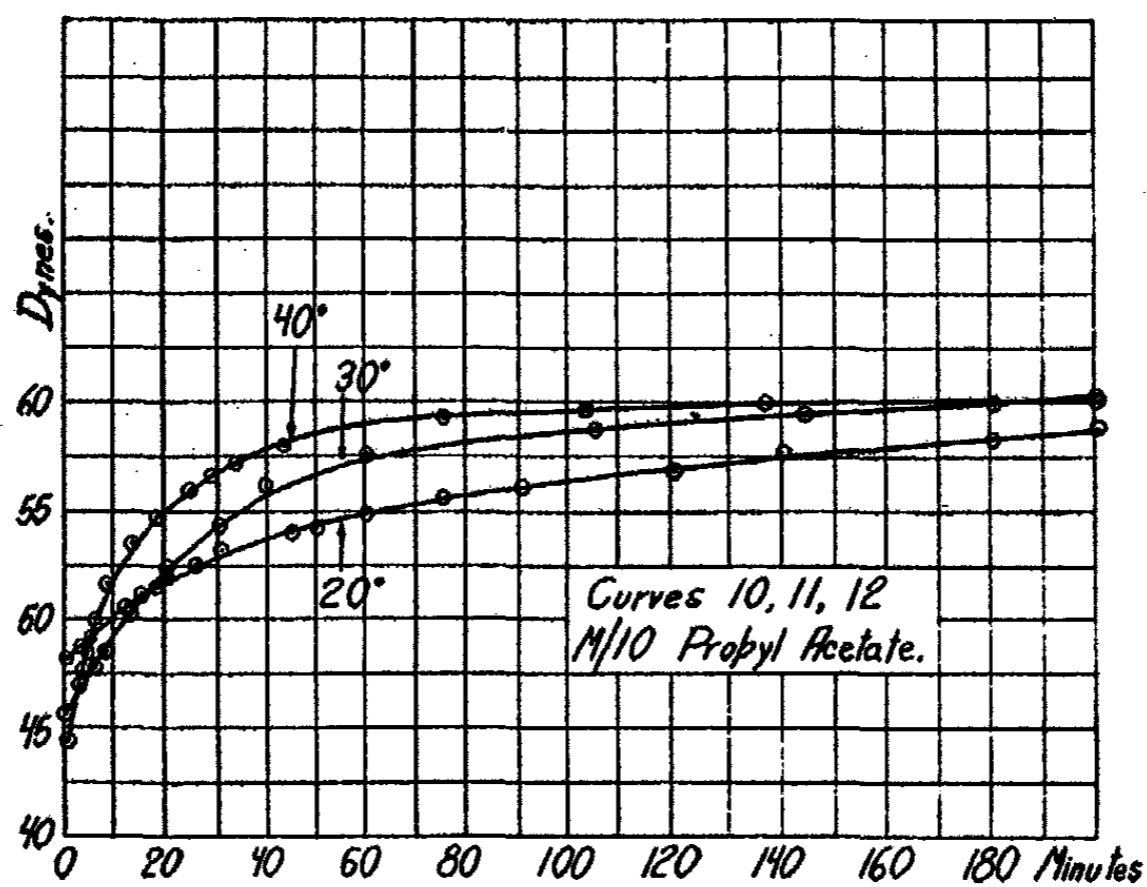
Solutions of Methyl Acetate. A molar solution of methyl acetate was used in several experiments intended as a more careful study of the rate of increase, and also of the effect of agitation in causing the drop from a maximum to a minimum surface tension. The results of a typical experiment with this solution are shown in Curve 9.

During the first two hundred and seventy-six minutes there was no agitation, and the surface tension increased from 47.5 dynes to 60.6 dynes. Then

the surface was agitated, by drawing it slowly up and down the tube once, after which a reading was taken. Then the liquid was again drawn up and down once, and a second reading was taken. This was repeated six times.

Manifestly the effect of agitation is cumulative and would finally result in a value practically the same as the initial reading.

Solutions of Propyl Acetate and Temperature Effects. Numerous experiments were carried out with solutions of this material in an attempt to find out the effect of different temperatures on the rate of the surface tension change.



The initial readings show, as was to be expected, the lowest surface tension at the highest temperature and the highest surface tension at the lowest temperature. Whatever the change which produces the increasing surface tension, it proceeds faster the higher the temperature. It looks as though we had reached the equilibrium condition at 40° after about 140 minutes. But the surface tensions at the lower temperatures are still ascending. The 30° curve crosses the 40° curve after 185 minutes and the 20° curve is gradually approaching that for 30°. We believe it will ultimately cross it. In short we feel justified by experiments in believing that the final equilibrium surface tension will be higher, the lower the temperature.

Quantitative Study. We felt that this phenomenon of rising surface tension was worth investigating quantitatively. It was necessary to choose one substance with which to work. It seemed desirable that the substance should show the phenomenon in as marked a degree as possible, that is, its solutions should have a surface tension much different from that of the solvent, water. It should be soluble enough to permit the study of a wide range of concentra-

tions; it should have a much higher vapor pressure than water, and not be readily hydrolyzed. Ethyl acetate was chosen as the solute best fulfilling these specifications.

Purification. Our stock ethyl acetate from the U. S. Industrial Chemical Co., was fractionated and that portion distilling over between 76.9° and 77.2° was reserved for further fractionation. After drying over phosphorous pentoxide for several hours this fraction was poured off and redistilled. A large amount which came over at nearly constant temperature was collected and preserved in a glass-stoppered bottle. The boiling point corrected to 760 mm. pressure varied from 77.11° to 77.20° . For this correction use was made of the dt/dp values obtained by J. Wade and R. W. Merriman.¹ The boiling point which they observed for pure ethyl acetate at 760 mm. was 77.15° . We found the density of our ester to be .9003 at 20° , which compares favorably with the density of .9005 recorded by Wade and Merriman for the same temperature.

A contraction in volume occurs when ethyl acetate dissolves in water and this contraction must be taken into account in making up solutions of definite concentration. We spent more time than we should have over this, actually determining experimentally this contraction. The details would not be of any general interest. We satisfied ourselves that making up solutions by diluting measured volumes of ester to calculated volumes of solution did not introduce a perceptible error in our results.

If the density of the vapor phase, air saturated with water and ethyl acetate, is much different from air saturated with water only, an error is introduced. (See formula $(\gamma = \frac{1}{2} \text{hr}g (D-d))$). The density of air at 20° saturated with water vapor is 0.0012. We made numerous determinations experimentally of the density of the vapor phase, air saturated with water and ethyl acetate over an $M/2$ ethyl acetate solution. The average of our results was, 0.001256. Error resulting from neglect of this correction was clearly negligible and so we used, $d = 0.0012$ throughout.

Ethyl Acetate. The following curves obtained with half molar ethyl acetate to show the type of rise we obtained and the limits within which one may expect to reproduce results.

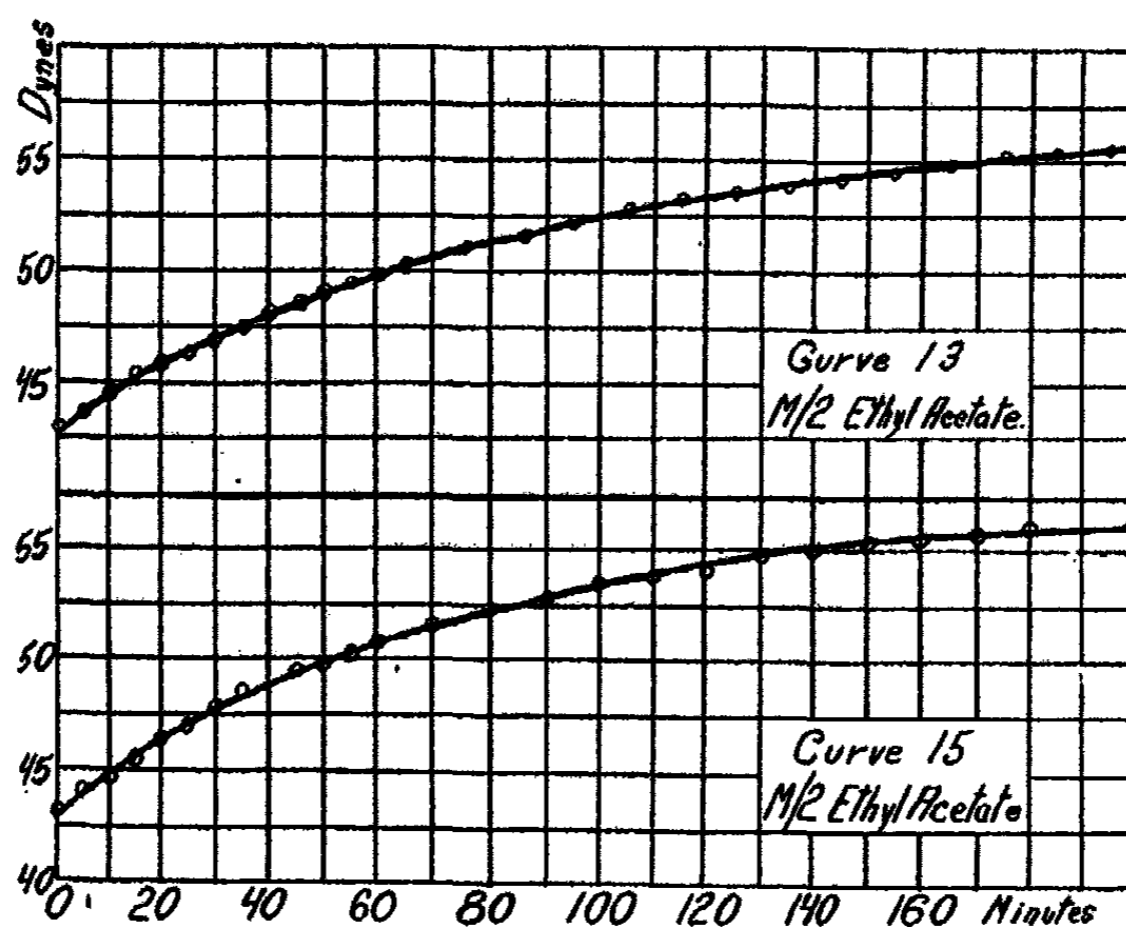
Agitation, by means of blowing and drawing, after each maximum value, caused the surface tension to return nearly to its original minimum value from which the usual rise again took place.

Curves 13 and 14 were obtained with both arms of the capillarimeter open to the air, while for curve 15 loose caps were hung over the open ends. The fact that these three curves are nearly identical is explained by the fact that the caps fitted loosely, allowing vapor to diffuse out as rapidly as it diffused up through the capillary.

We next joined the two arms of the capillarimeter with a piece of tightly-fitting, black gum, rubber tubing, and carried out the experiment resulting in curve 16. We thought that under these conditions the vapor phase would soon become saturated with the vapors of water and of ethyl acetate. An

¹ J. Chem. Soc., 101, 2438 (1912).

equilibrium would thus be reached at the meniscus, and there would be no further concentration change in this and consequently a constant surface tension would be obtained. The curves show that the presence of the rubber tubing made no noticeable difference. The rise proceeded at the same rate as before. The experiment was repeated many times but always with the same result. Even after being thus closed in the capillarmeter for several days the



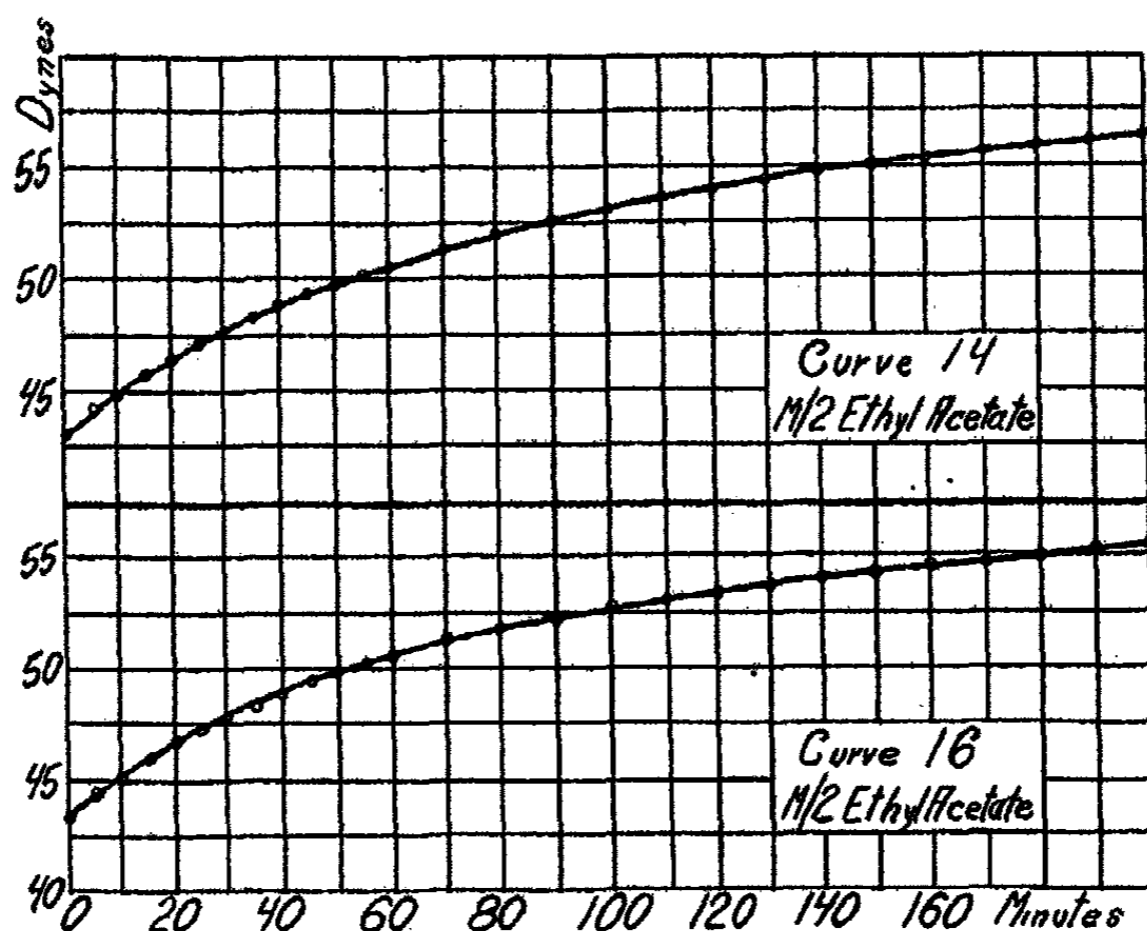
solution would show the usual rise from the minimum, obtained after an agitation, to a maximum value. This almost caused us to abandon the theory that the rise was due to evaporation of the ethyl acetate from the meniscus faster than it was replaced by diffusion from the interior.

Fortunately it occurred to us that perhaps the ethyl acetate was dissolving in the rubber, thus preventing the establishment of equilibrium at the meniscus.

Two pieces of black gum rubber tubing about three centimeters long, equipped with platinum hooks, were carefully dried and weighed. One of them was then suspended from a glass rod in a flask above distilled water, as shown in Fig. 5. The second piece was suspended above a half molar solution of ethyl acetate in a similar flask. After being in contact with the vapors in the flasks for some hours, the rubber tubes were again weighed. The original weight of the rubber tube which was suspended above water was 1.5420 gms. After eight hours and fifty-three minutes of contact with water vapor it weighed 1.5500 gms. The original weight of the rubber tube which was suspended above M/2 ethyl acetate was 1.5950 gms. After eight hours and fifty-three minutes of contact with the vapor above the solution it weighed 1.7500 gms., a gain of .1550 gms.

After twenty-three hours and thirty minutes the tube above the water showed a gain of .0165 gms., while the tube above the solution of ester for the same length of time, showed a gain of .1850 gms.

A similar experiment carried out with water and an aqueous solution of propyl acetate gave very similar results. Evidently rubber will take up large amounts of ester vapors. After being exposed to the air for several hours the



tubes again showed their original weights. This explains the fact that the closing of the capillarmeter with a rubber tube in experiment 16, caused no change in the rate of increase of surface tension. The tube did not close the system and prevent evaporation. It might as well not have been there.

Vapor lost by Diffusion. In order to find out whether or not the amount of vapor absorbed by the rubber tube was comparable with the amount which would ordinarily evaporate and diffuse out of the capillary tube of a capillarmeter, the following experiment was carried out. A capillary tube with a bulb at one end, as shown in Fig. 6, was filled with half molar ethyl acetate solution to within about 3.3 cm. of the top. Sixteen hours were allowed for the drainage and drying of the capillary walls above the meniscus. Owing to the short length of the tube above the meniscus, more ethyl acetate should evaporate and diffuse from this tube than from the capillary of any capillarmeter used. After the sixteen hour period the meniscus was 3.50 cm. from the top. The instrument was then weighed after different time intervals with the following results.

| | |
|---------------------|------------|
| Loss after 10 hours | .0002 gms. |
| " " 15 " | .0005 " |
| " " 48 " | .0015 " |
| " " 72 " | .0027 " |

After seventy-two hours the meniscus was 4.06 cm. from the top, a fall of about .56 cm.

This experiment proves that the amount of ethyl acetate and water which will evaporate and diffuse from a capillary, of the size used in our capillimeters, is much less than the amount which the rubber tube is capable of absorbing in the same time.

Closed Capillarmeter. In order to close completely the capillarmeter and obtain saturation of the vapor and equilibrium at the meniscus, we made use of an instrument constructed as shown in Fig. 4. With the stopper out the system was open; with it in, it was truly closed.

The following curve is representative of the many which we obtained with solutions of different esters and alcohols in capillarmeters of this type.

In another experiment carried out in the same capillarmeter at 20° with half-molar ethyl acetate, the initial surface tension was 42.3 dynes. After one and a half hours with the system open the value increased to 54.0 dynes, the system was then closed and after another hour and a half the surface tension had decreased to 42.4 dynes. The system was again left open for one and a half hours, and the surface tension increased to 54.4 dynes. The glass stopper was then inserted, and twelve hours later the surface tension was 40.2 dynes.

The fact, that the surface tension stopped increasing and started to decrease as soon as the system was closed with a glass stopper, must be due to the gradually increasing concentration of the ester in the vapor phase. It was often observed that the value obtained for the surface tension of a solution, after the capillarmeter had been closed for some time, was lower than the value shown by the solution immediately after being poured into the capillarmeter. This is probably due to the difficulty of obtaining a reading of the position of the meniscus, before a slight rise has taken place.

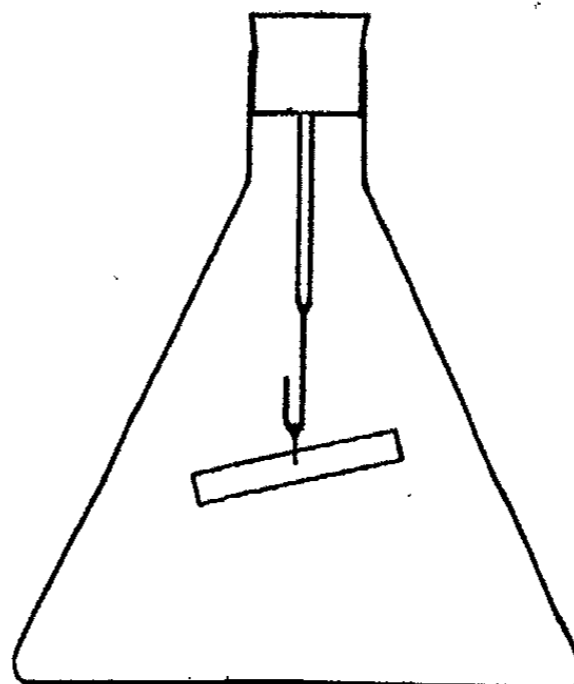


FIG. 5

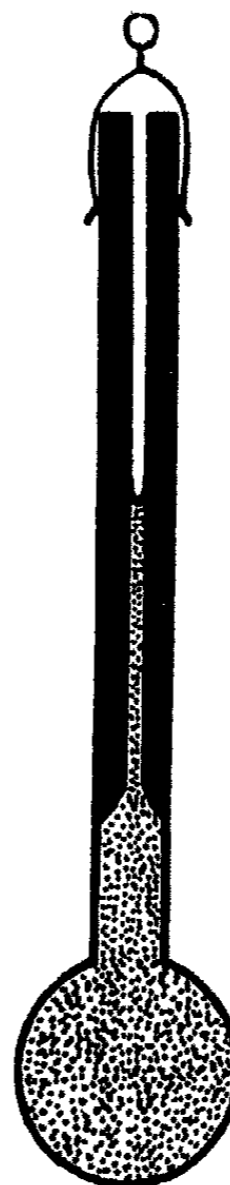
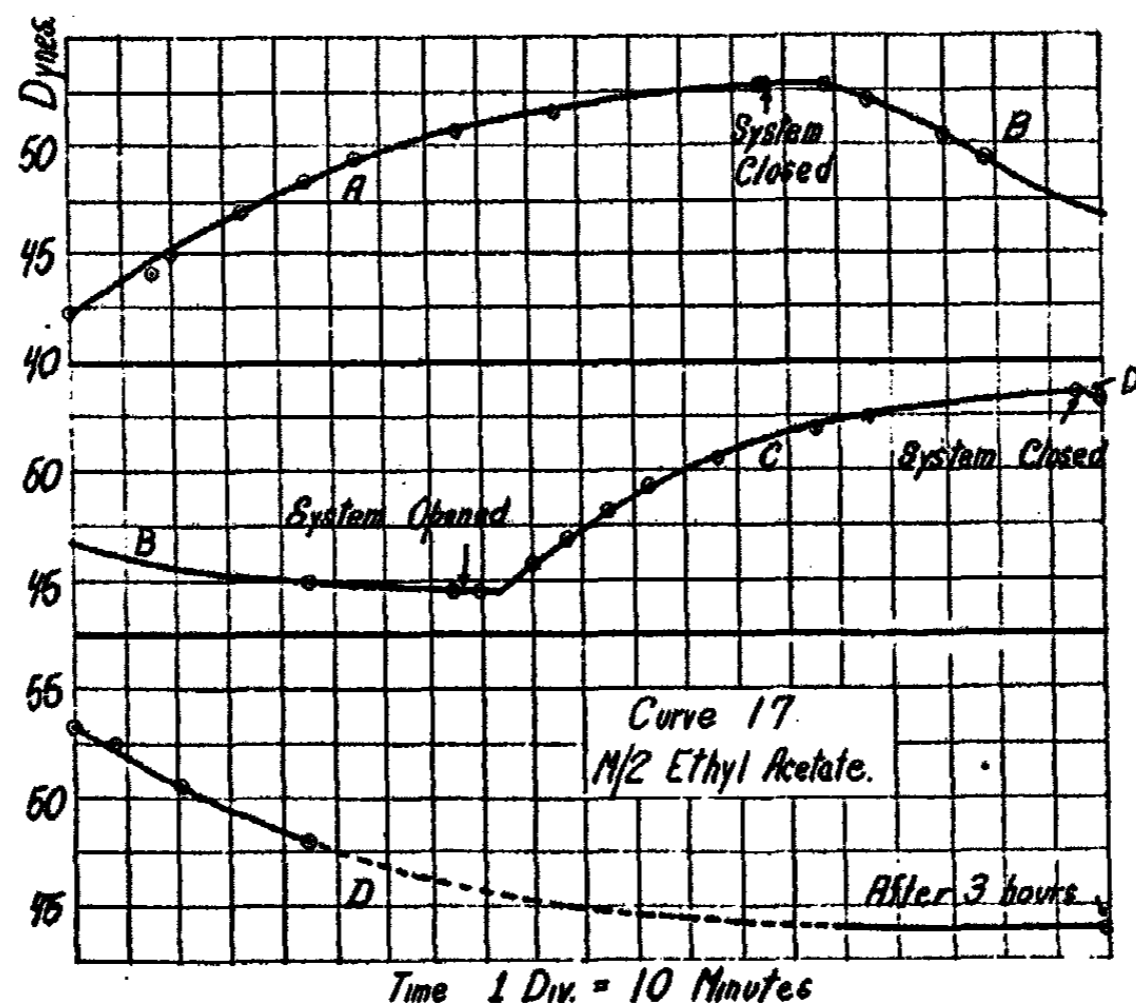


FIG. 6

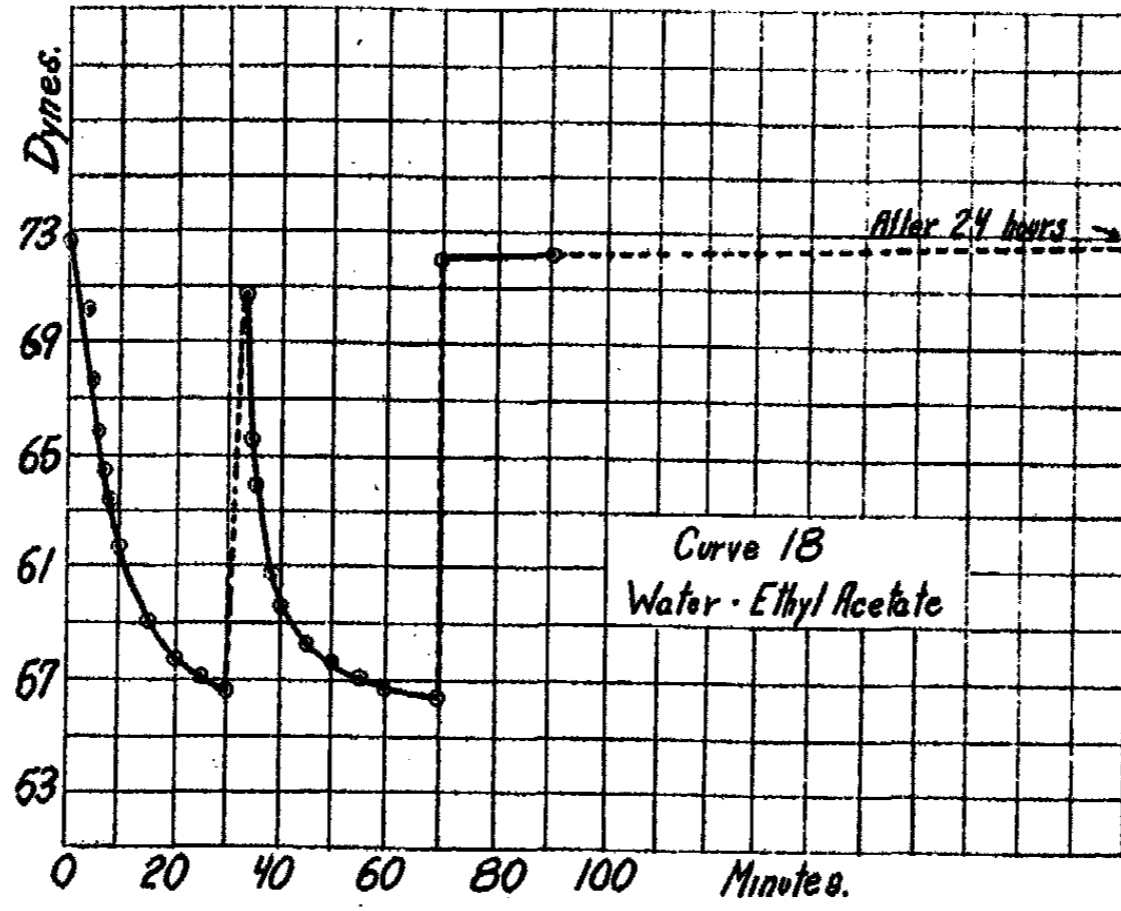
Experiments in Side Arm Capillarimeter. Convincing evidence that the extremely small amount of ethyl acetate which does evaporate and diffuse through the capillary in one of our instruments is sufficient to cause the observed change in surface tension is given by the following experiment. A capillarimeter was constructed with a side arm attached above the capillary tube, as shown in Fig. 3. Pure water was placed in the main part of the in-



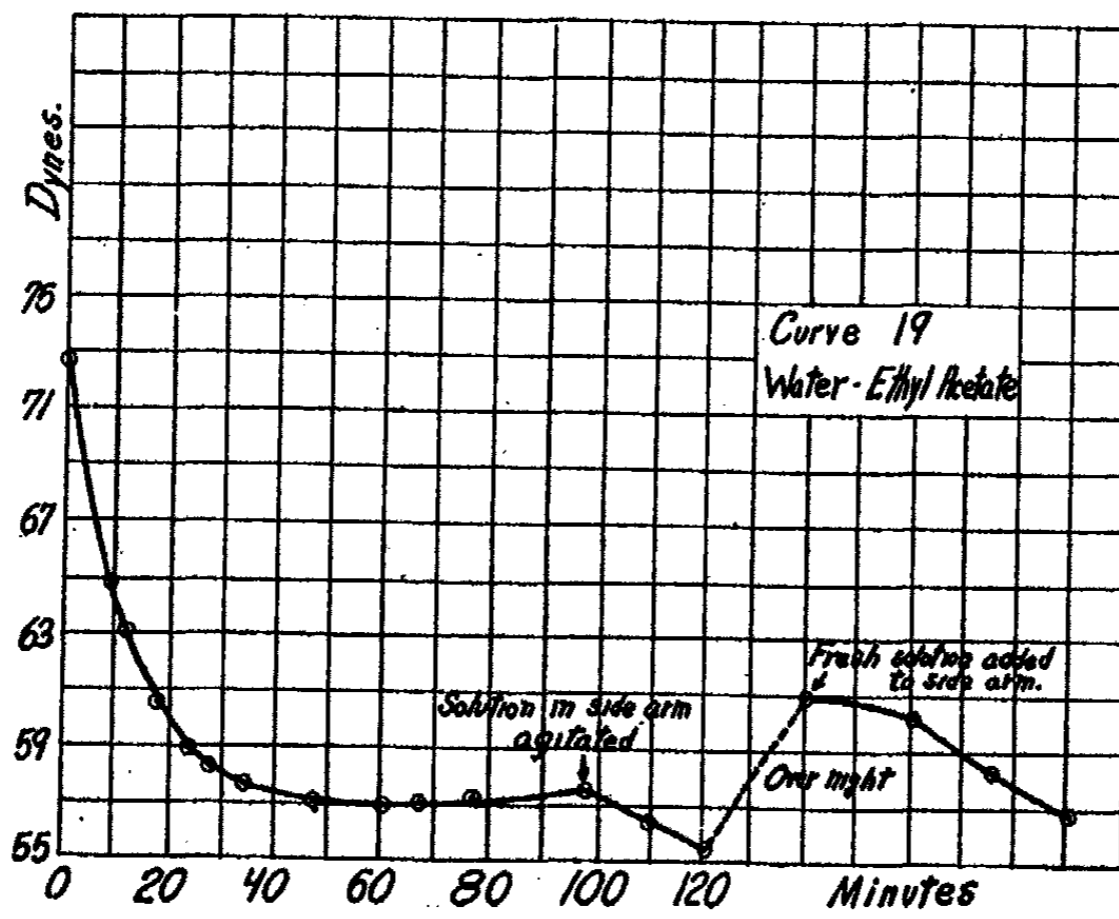
strument and its capillary rise noted. Half molar ethyl acetate was then placed in the side arm and the following curve was obtained.

The fall is obviously due to the evaporation of the ethyl acetate from the side arm, diffusion through the capillary and its solution in the surface. After 30 minutes, when the value 56.6 dynes had been reached, the solution in the capillary was violently agitated with the result that the surface tension rose to 70.8 dynes. This was evidently because the comparatively concentrated layer in the meniscus got stirred into the body of the liquid. At 70 minutes we removed the ethyl acetate solution from the side arm and agitated the solution as before, we immediately got a value of 72.1 dynes which rose to 72.6 in 24 hours.

We have shown that the actual amount of ethyl acetate which would evaporate and diffuse through our capillary tubes is very small, less than .0002 gms. in ten hours or about .00001 gm. in thirty minutes in a tube the length of this one. Yet this extremely small amount was sufficient to cause a drop in surface tension of sixteen dynes. This is a convenient and striking way to demonstrate the known fact that minute traces of some substances produce marked effects on surface tension.



Rise after Minimum Value. In many of the experiments carried out as described for Curve 18, it was observed that after the minimum value was reached a slight increase would take place. More careful investigation showed that this increase always took place if the experiment was continued long enough, providing that the liquid in the side arm was a solution of the ester and not the pure ester. The magnitude of the changes involved is shown in the following characteristic curve.



This behavior is readily explained. The meniscus is gaining ethyl acetate due to evaporation from the side arm and is losing it as it diffuses downward into the liquid. Simultaneously the evaporation in the side arm is diminishing due to the diminishing concentration in that surface. These effects all balance at the minimum apparent on the curve at 60 minutes. After this the meniscus loses by diffusion faster than it gains from the side arm. But when we renewed the surface in the side arm by agitation, the curve took a downward trend again.

Diffusion through Gases. Measurements such as these could readily be developed into a convenient method of studying the rates of diffusion through gases in capillary tubes. They could also be used to measure the rates of diffusion from the surface into the body of the liquid.

Diffusion through Liquid. In an ordinary open capillarimeter (Fig. 2) we placed some half-molar ethyl acetate. We then carefully inserted some pure water in the capillary tube, enough to cover the solution meniscus with a water layer about one centimeter thick. The only way in which the ester can affect the surface tension of such a system is by diffusion up through the water to the meniscus. Of course a little of the solution is likely to stick to the walls of the tube and thus contaminate the water as it is poured in. With careful manipulation, however, such effects are very small. Several experiments of this sort, at 20°, did not show any change in several hours. In order to hasten diffusion we then carried out experiments at 40°. The following results are typical.

| Time elapsed. | Surface tension |
|-------------------|-----------------|
| 0 minutes | 68.8 dynes |
| 47 " | 68.4 " |
| 215 " | 68.5 " |
| 1080 " | 68.7 " |
| solution agitated | 52.3 " |

The surface tension remains nearly that for pure water, not enough ester molecules diffusing through the water in over eighteen hours to cause any lowering. After this interval the solution was agitated by drawing it down out of the capillary several times. Enough ester was thus mixed with the water to cause a large lowering in the surface tension. Evidently diffusion through the liquid phase must be very slow. This method is capable of development and may be of some practical value.

Incidental Observations

It was our original purpose to discover, investigate and report as many sources of error as possible connected with the measurement of surface tension by the capillary tube method. We shall, therefore, now present a few incidental observations which were made.

Drops. It often happens that a drop (ring of liquid) forms at some distance above the meniscus. Following is a description of one instance. It occurred when working with half molar propyl acetate. In the initial reading the top of the meniscus, A (Fig. 7) stood at 13.000, while the bottom of the

drop, B, stood at 13.200 on our cathetometer scale. Twelve minutes later the meniscus A had ascended to A', 13.180, while the drop had remained stationary. Immediately after taking this reading the drop B suddenly disappeared and at once the meniscus rose to A'', 13.260, slightly above the place where the top of the drop had been. The drop is formed by drainage of the solution left on the walls after wetting, and just as in the well-known phenomenon of "tears on strong wine," it rapidly becomes

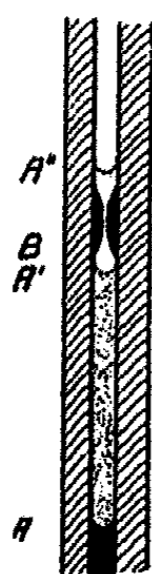


FIG. 7

more nearly pure water by the evaporation of the ester. Evaporation is going on at the surface of the meniscus also, and, as a result, the meniscus rises until it approaches near enough to the drop to draw it to itself, or to be drawn up by the drop, resulting in a sudden increase in surface tension due to the more nearly pure water of which the drop is composed.

The same phenomenon has often been noted in a slightly different form. The whole length of capillary having been wet by the solution, a drop was seen to form as at A in Fig. 8. The tube being a rather wide one the drop began to fall slowly. The fall was followed by the telescope and it was noted that when it was within a few millimeters of the meniscus it suddenly disappeared



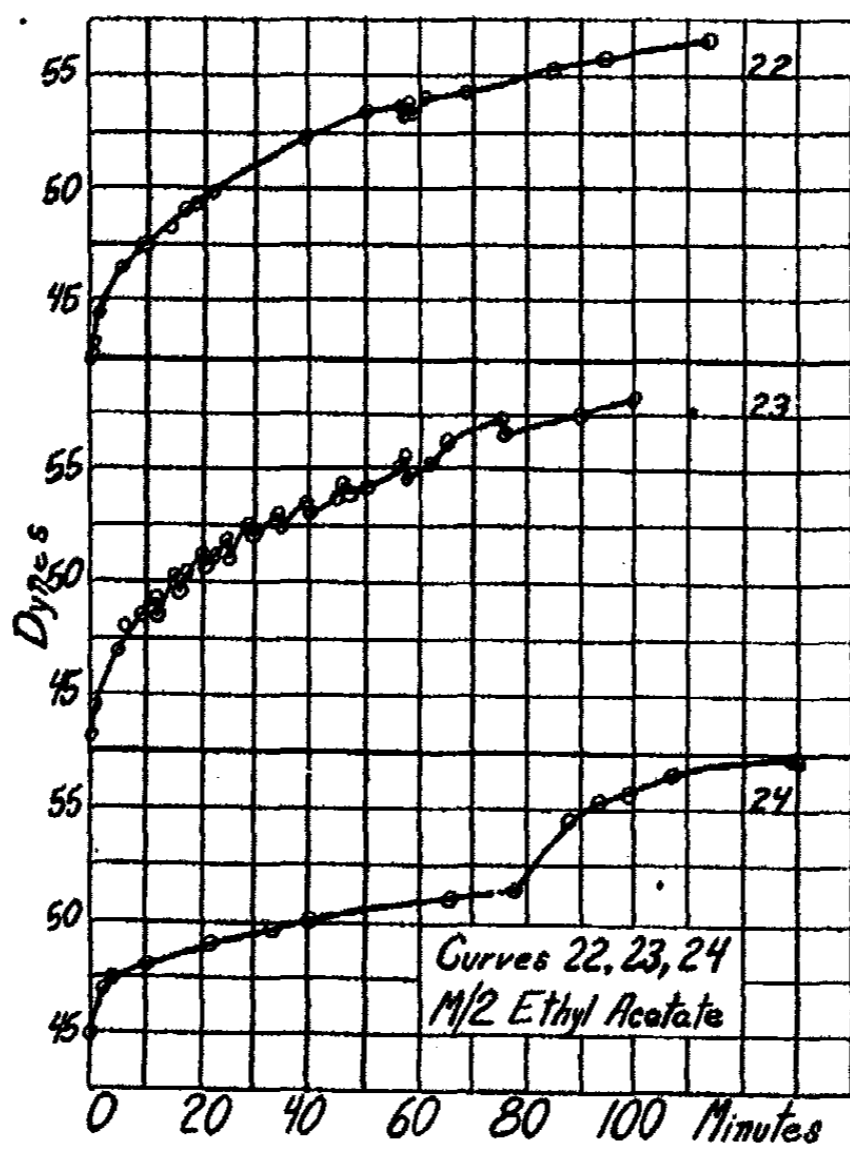
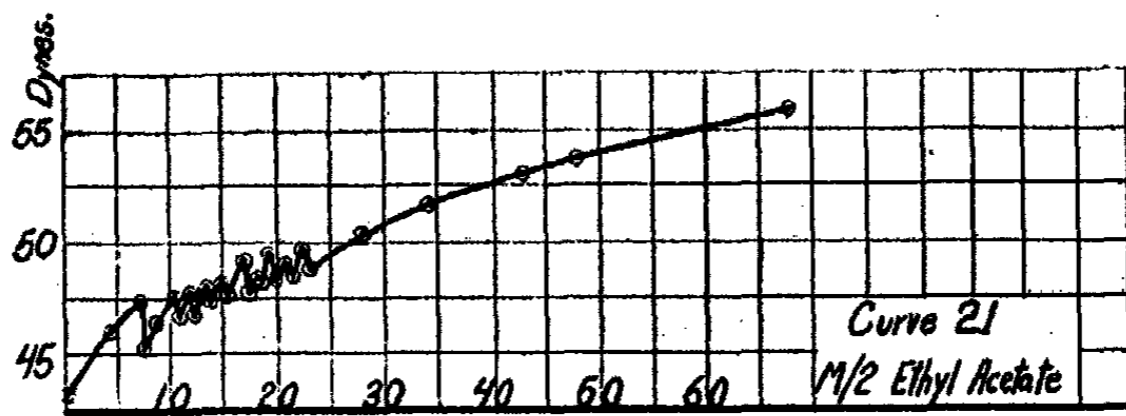
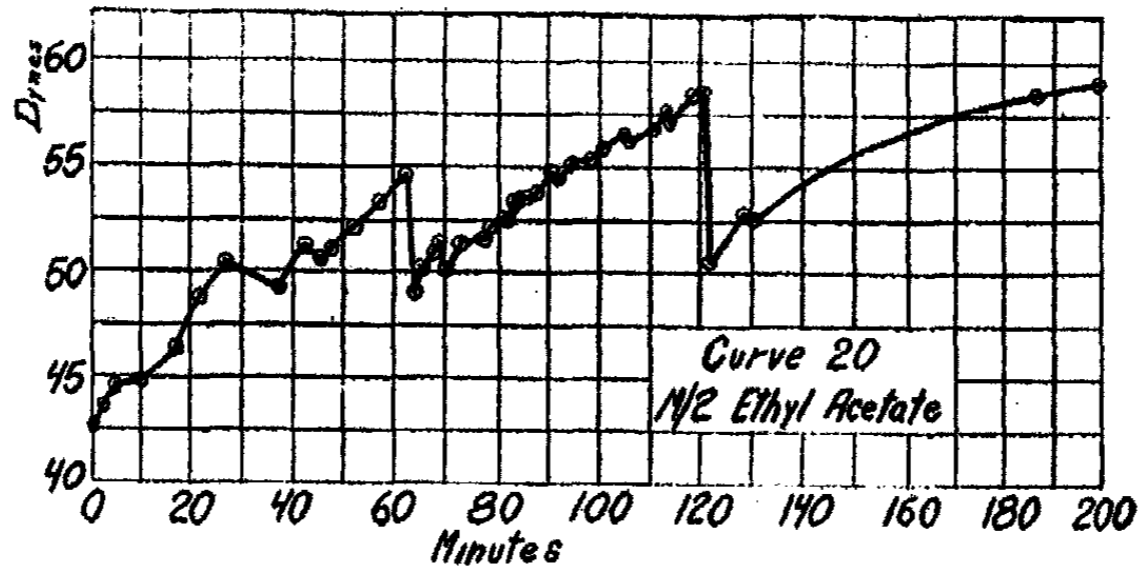
FIG. 8

downward into the meniscus, which in turn, ascended quickly to a new height. Not nearly enough liquid descended in the drop to account for the rise noted. During its gradual fall the drop had become more nearly pure water, due to the evaporation of the ester, and when near enough to the meniscus to be pulled into it, it simply exerted its proper surface tension.

It is probable that small drops are formed on the walls of the tube above the meniscus fairly often. They may be too small to be seen, but large enough to be the cause of the rapid increases sometimes noted, and unaccounted for in any other way.

Throbbing. Many of our experiments have failed to give us a smooth, uniform rise. During its ascent, the meniscus would often pause, fall rapidly and then rise slowly as before. When a point, slightly higher than the one from which the fall had taken place before, was attained, another drop followed by another rise, took place. This phenomenon was often repeated many times in the course of an experiment. The range of these pulsations varied, from a small fraction of a dyne in some instances to four or five dynes in other. We found it convenient to refer to this behavior as a "throbbing."

The frequency of this throbbing, as well as the range, varied a good deal. Sometimes several minutes would elapse between throbs, while at other times they would follow each other in rapid succession. Constant vigilance was the price of a numerical record of this phenomenon. Several experiments were carried out, during which, careful watch was kept on the meniscus, a reading being taken every time that it changed the direction of its motion. Several of these records will be given to show the extreme lack of regularity in these variations.



This throbbing was evident in probably thirty per cent of the experiments which involved an increasing surface tension. It seems much more apt to occur if the increase starts out rapidly than if it starts slowly. It very seldom occurs in an experiment involving a decreasing surface tension, although we have noted it in a few such experiments.

As a possible explanation we offer the following suggestion. We have learned by experience that it is exceedingly difficult to make the surface of a capillary tube (or any other surface) strictly clean, and yet more difficult to keep it so, even for a short time. It is perfectly possible that, in spite of all our precautions our tubes were not entirely clean. Then as the meniscus rises it will dissolve contamination until the surface acquires a lower surface tension, compelling a fall. Its subsequent ascension is not hindered in the interval through which it dropped for the walls were cleaned by the motion of the liquid. Therefore the meniscus rises rapidly and uniformly through the distance it fell, and rises higher until it gathers up more contamination; enough to produce the next fall.

Again the phenomenon may be due to molecular rearrangements in the surface film. This idea of definite molecular orientations is truly fascinating. If we give free rein to our imagination, as seems to be the fashion just now, we may conceive that the molecules of ethyl acetate in a dilute solution travel around in schools, or molecular swarms, and when such a swarm arrives at the meniscus there is a corresponding drop in the surface tension. This idea is not without support. For instance, J. M. Johlin¹ makes the statement: "Evidence of rearrangements at the surface is indicated by the frequent throbbing or pulsating of the meniscus, without necessarily resulting in any immediate change in surface tension—a fact invariably observed in all experiments with a wider capillary."

We are inclined to be conservative and, while admitting the possibility of such an explanation, prefer not to commit ourselves at present.

Effect of Size and Shape of Capillarimeters. It became evident to us that, although the initial, minimum values were easily reproducible, the rate of increase of surface tension varied with different capillarimeters. With instruments of nearly the same shape and dimensions the differences in rate were not great. But with capillarimeters of radically different type greater variation is evident. For example, the rise noted in capillary D when used in the form illustrated in Fig. 2 was more rapid and a higher maximum was reached than when the tube was used in the form illustrated by Fig. 4.

This variation is adequately explained on the basis of the evaporation theory. The air and vapor in the tube above the meniscus is stagnant, that is, it is not readily removed by external air currents. It is natural to suppose that it is more stagnant in an instrument of the type shown by Fig. 4 than in the kind illustrated by Fig. 2, for in the former case there is only one opening to the atmosphere while in the latter case there are two.

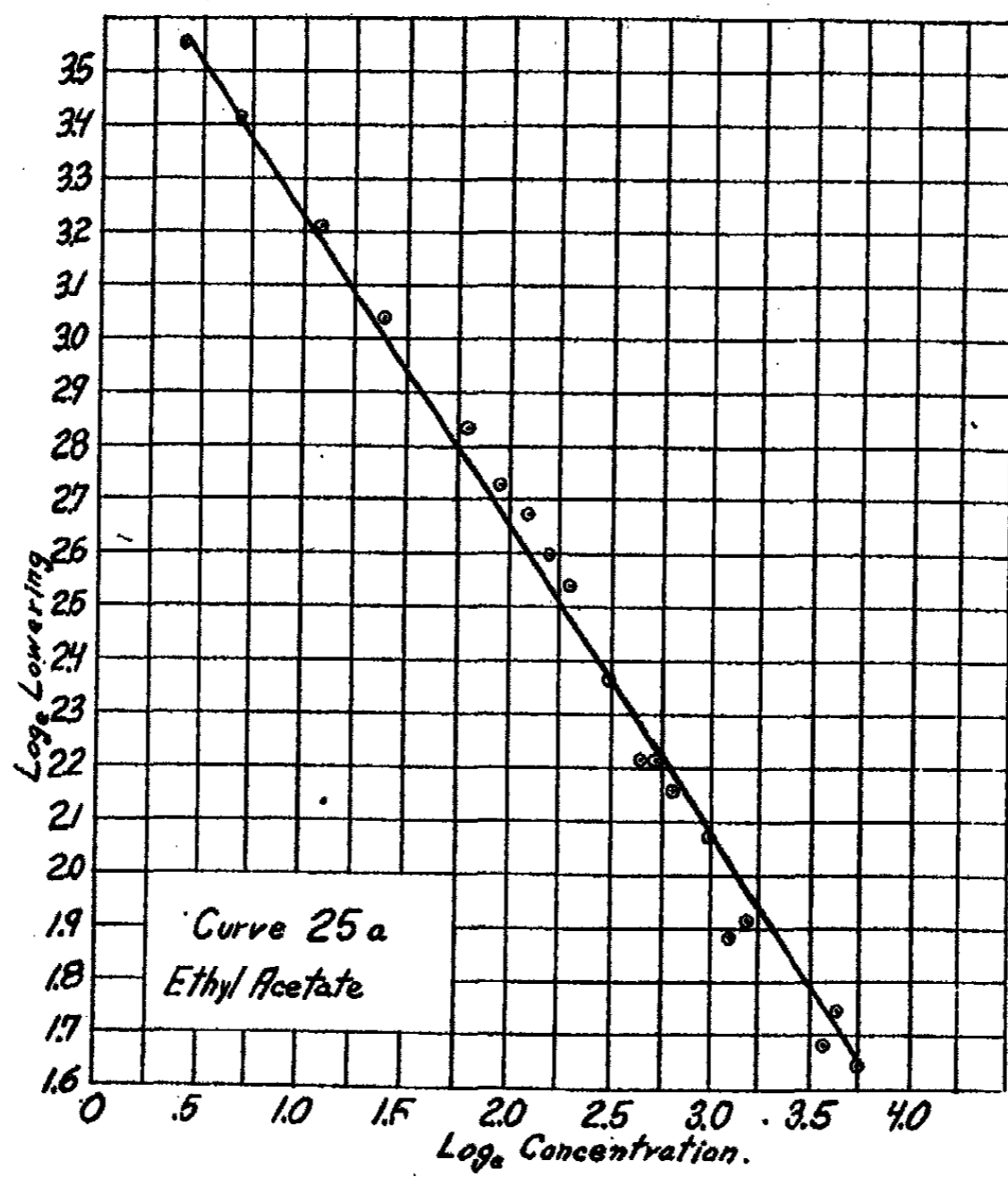
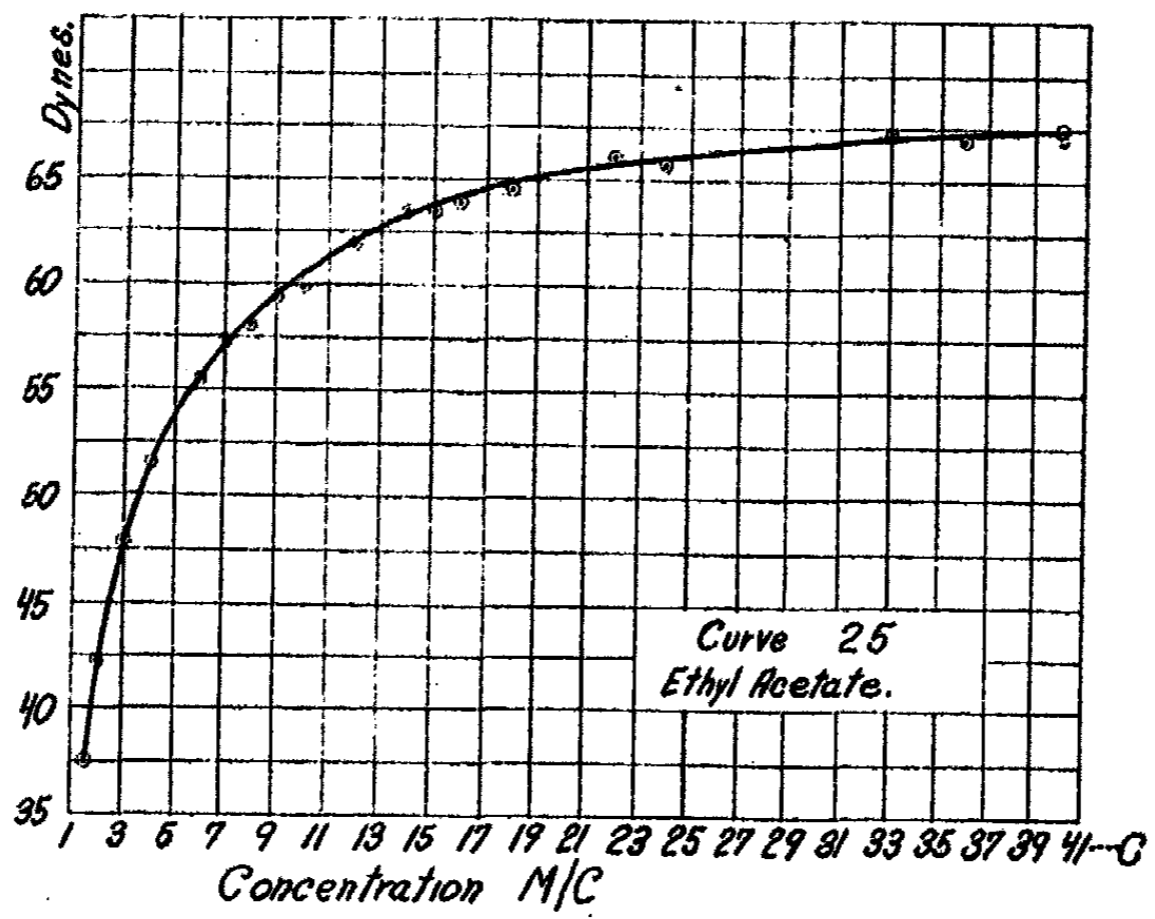
¹ J. Phys. Chem., 29, 282 (1925).

It is more difficult, however, to account for the fact that in capillarimeters which are alike except for the diameter of the capillary, the phenomenon proceeds more rapidly in the capillary of the smaller diameter. If simple diffusion of gases was the controlling factor in the velocity of the change we would expect it to be greater in the larger tube. At present we have no plausible explanation to offer.

Concentration in the Surface. We carried out experiments in which we determined the true surface tension of ethyl acetate solutions of different concentrations. In obtaining the true surface tensions of these solutions two methods are available. Experience has shown us that the best method is to use a closed capillarimeter and to allow sufficient time for the atmosphere to become saturated with the vapor of the solution. The second method is simply to note the initial minimum value before any change with time has taken place. This method usually gives values slightly higher than the first, due to the difficulty of determining the initial point of a slowly moving meniscus. With careful but rapid manipulation, however, it is possible to check, very closely, results by the two methods. In the following table the method or methods used, are stated in each case. Several different capillarimeters were used in these experiments, no difficulty being experienced in checking minimum values with the different instruments. Temperature $20.0^{\circ} \pm 0.1^{\circ}$.

| Concentration Molar | Surface tension | Method | Lowering from water value | |
|------------------------|-----------------|------------|------------------------------|------|
| M/1.5 | .6666 | 37.6 dynes | open tube | 35.1 |
| M/2 | .5000 | 42.2 " | both methods | 30.5 |
| M/3 | .3333 | 47.9 " | both methods | 24.8 |
| M/4 | .2500 | 51.5 " | both methods | 21.2 |
| M/6 | .1666 | 55.6 " | closed tube | 17.1 |
| M/7 | .1428 | 57.4 " | open tube | 15.3 |
| M/8 | .1250 | 58.1 " | both methods | 14.6 |
| M/9 | .1111 | 59.3 " | closed tube | 13.4 |
| M/10 | .1000 | 59.9 " | open tube | 12.8 |
| M/12 | .0833 | 61.9 " | open tube | 10.8 |
| M/14 | .0713 | 63.5 " | open tube | 9.2 |
| M/15 | .0666 | 63.5 " | open tube | 9.2 |
| M/16 | .0625 | 64.0 " | both methods | 8.7 |
| M/18 | .0555 | 64.7 " | both methods | 8.0 |
| M/22 | .0454 | 66.1 " | open tube | 6.6 |
| M/24 | .0416 | 65.9 " | closed tube | 6.8 |
| M/33 | .0333 | 67.3 " | open tube | 5.4 |
| M/36 | .0277 | 66.9 " | closed tube | 5.8 |
| M/40 | .0250 | 67.5 " | both methods | 5.2 |

Plotting these results we obtain Curve 25. We can read off from this curve directly the concentration of the solution which must correspond to any particular surface tension. It would be going too far to make the simple assumption that the concentration at the meniscus is the same as in the interior of the



liquid under these conditions. But it may be. Whatever the conditions actually are we have here an interesting relationship which will be of help in elucidating them.

H. Freundlich¹ gives an equation connecting surface tension lowering with concentration.

$$\Delta = \frac{\gamma_m - \gamma_1}{\gamma_m} = Kc^{1/n}$$

Where Δ is the lowering of surface tension to be expected for any concentration c ; γ_m is the surface tension of the pure solvent; γ_1 the surface tension of the solution; K and $1/n$ are constants. That our experiments agree essentially with the formula is shown by the nearly straight line obtained when the logarithm of the concentration is plotted against the logarithm of the lowering. Curve 25a.

Rate of Increase. We have advanced the theory that increase of surface tension with time is due to evaporation of solute from the surface faster than it is replaced by diffusion from the body of the solution. Certain deductions from this theory are possible. When an apparent maximum surface tension is reached the rate at which the surface is losing solute by evaporation is equal to the rate at which it is gaining solute by diffusion. But this must be only an apparent maximum for, given time enough, practically all solute will reach the surface and will evaporate. The true maximum must always be the surface tension of pure water. Replenishment of the surface must be directly proportional to the concentration from which diffusion takes place. Consequently the increase in surface tension should be most rapid at the beginning and should fall off with time. This deduction has been abundantly verified.

It follows that when a solution of greater concentration, say $M/2$, has reached a point where it shows a surface tension corresponding to a lower concentration, say $M/5$, the adjacent layers have been impoverished and diffusion must proceed through a greater distance. Therefore the rate at which the surface tension of this solution increases should be less than the initial increase shown by an $M/5$ solution. We put this deduction to the test of experiment.

Our deduction is well justified. At the expiration of 60 minutes the $M/2$ curve showed the surface tension corresponding to an $M/5$ solution. Its slope at this time is obviously less than the initial slope of the $M/5$ curve. At the expiration of 60 minutes the $M/5$ curve showed a surface tension corresponding to an $M/10$ solution and its slope is less than the initial slope of the $M/10$ curve, and so on.

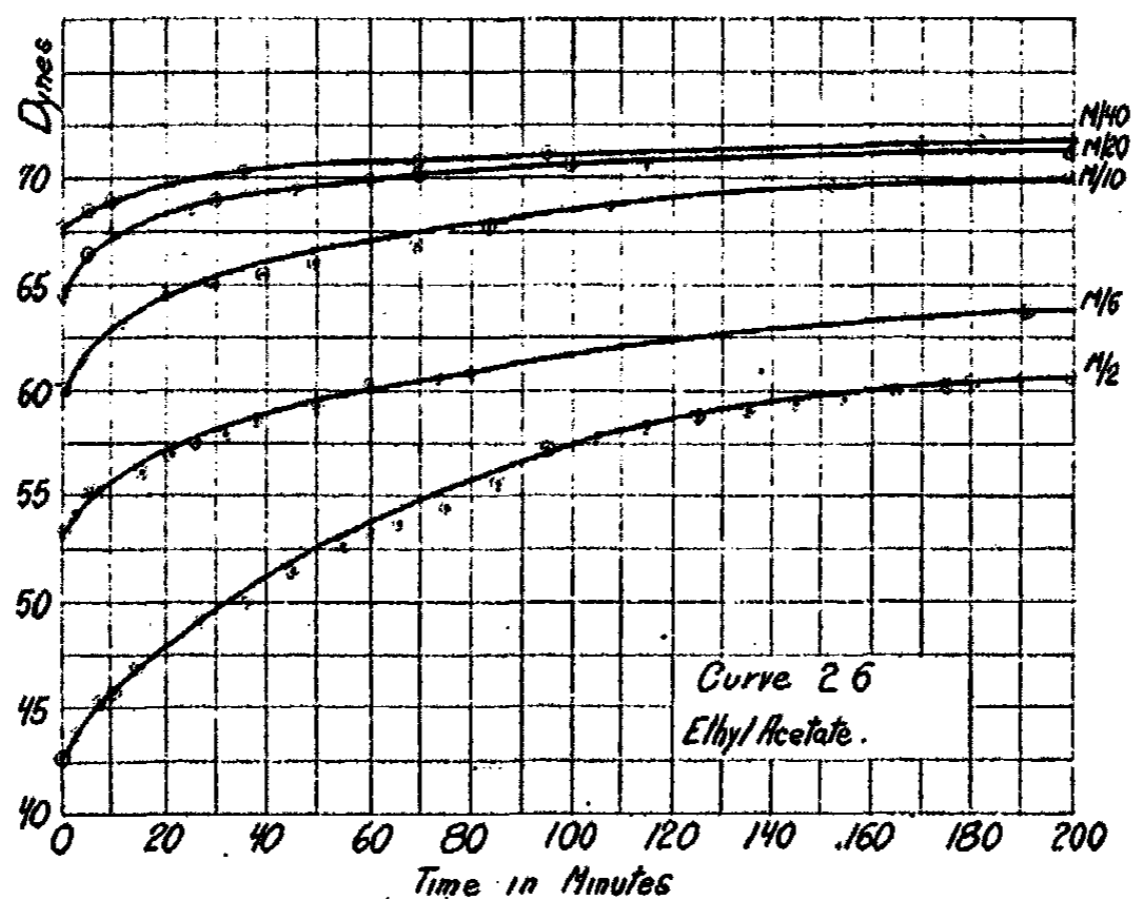
Hydrolysis. The substances with which we have worked hydrolyze, and if this occurs with sufficient rapidity our results give the surface tensions, not of solutions of our initial substances, but of the products of the hydrolysis.

We investigated this matter and found that the rates of hydrolysis varied greatly with different esters. In general, esters of lower molecular weight

¹"Kapillarchemie," 90 (1922).

hydrolyze faster than those of higher. For example, a solution of methyl acetate hydrolyzes more rapidly than a solution of ethyl acetate of the same molecular concentration.

We proved by experiment that a solution of ethyl acetate in water hydrolyzes very slowly, too slowly to invalidate any of the results we have reported.



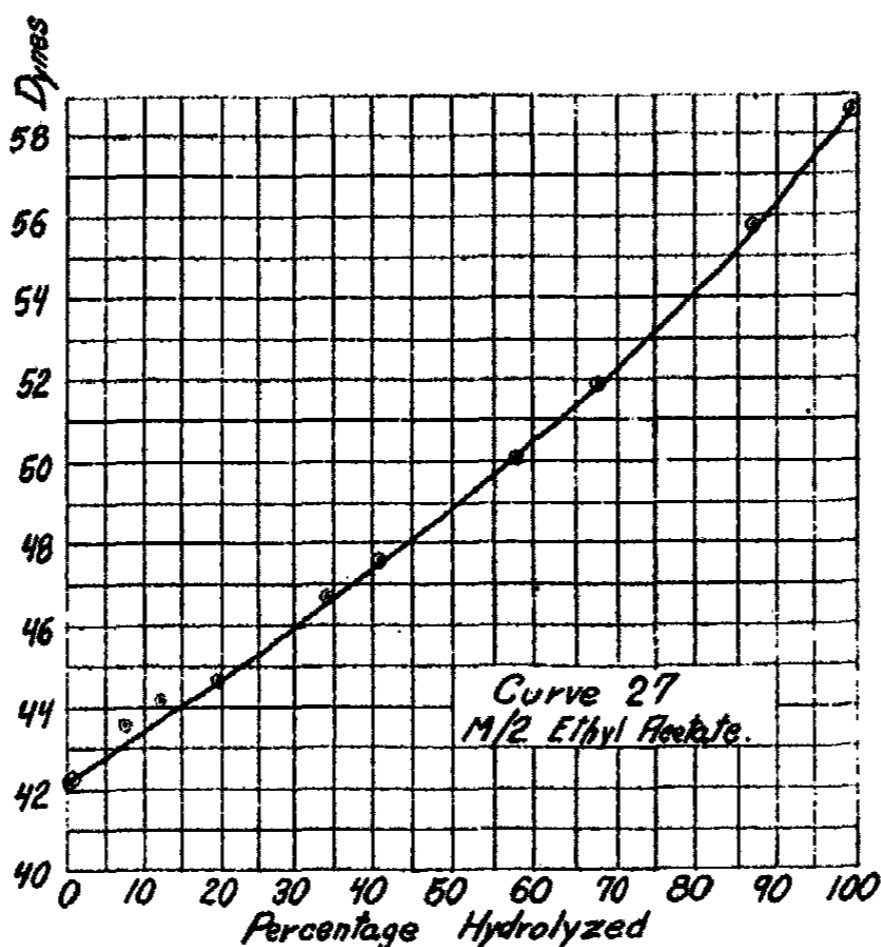
Two half molar solutions of ethyl acetate were made up and kept in glass stoppered flasks. These flasks were suspended in a constant temperature bath at $20.0^{\circ} \pm .5^{\circ}$. Samples were removed from time to time and titrated with standard barium hydroxide, using phenolphthalein as the indicator.

| Solution 1 | | | Solution 2 | | |
|--------------|-------|---------------------|--------------|-------|---------------------|
| Time elapsed | | Per cent hydrolyzed | Time elapsed | | Per cent hydrolyzed |
| 0 | Hours | .026 | 0 | Hours | .026 |
| 12 | " | .026 | 23.5 | " | .033 |
| 48 | " | .040 | 71 | " | .13 |
| 136 | " | .16 | 126 | " | .16 |
| 181 | " | .23 | 179.5 | " | .26 |
| 252 | " | .43 | 314 | " | .83 |
| 496.5 | " | 1.36 | 483 | " | 1.85 |
| 665 | " | 2.43 | 657 | " | 3.33 |
| 827 | " | 4.00 | 4689 | " | 86.0 |

During the last five months solution 2 was kept at room temperature, several degrees above the temperature of the first part of the experiment.

We ran surface tension determinations on this 86% hydrolyzed solution and found an initial value of 55.5 dynes which increased to 58.2 dynes in 13 hours. Thus, when the solution is hydrolyzed, the minimum value is higher and the maximum value is lower than when it is fresh and not hydrolyzed.

This experiment, and several others, showed us that surface tension of solutions of esters increases as hydrolysis progresses. It is therefore possible to plot a curve, surface tension against degree of hydrolysis, from which it



will be possible to read directly the degree of hydrolysis corresponding to any particular surface tension. Of course it will be necessary in making or using such a curve to deal only with the minimum or true surface tension of any particular solution. As has been explained, this is best obtained by the use of a closed capillarimeter.

We obtained data for such a curve by making measurements upon an M/2 ethyl acetate solution which we caused to hydrolyze at a convenient rate by warming. Care was taken to allow no change in concentration due to evaporation. The degree of hydrolysis was determined by the usual barium hydroxide titration, carried out simultaneously with the measurement of surface tension. The value corresponding to a completely hydrolyzed solution was obtained by making up a solution of ethyl alcohol and acetic acid in the proper proportion to form a 100% hydrolyzed solution. Titration showed that this solution corresponded to 99.8% hydrolysis.

This is capable of being developed into a method for measuring the degree of hydrolysis of solutions of esters. Experiment has shown us that the surface tension of solutions of substances such as ethyl acetate may be readily determined to within 0.4%, with ordinary instruments and technique. We ob-

served that as a half molar solution of ethyl acetate changed in hydrolysis from 0% to 100% the surface tension underwent a total increase of 16.5 dynes. Our measure of the hydrolysis by the surface tension method was then accurate to within approximately $\pm 2.4\%$. ($.4/16.5 \times 100 = 2.4\%$)

The rate of any chemical reaction, resulting in a sufficiently large change in the surface tension, can be followed by this method.

Summary

(1) The decrease of surface tension with time, of solutions of sodium oleate, sodium glycocholate, and glycerol, as observed by earlier workers, has been confirmed. We have demonstrated that the same phenomenon occurs with solutions of other substances such as, phenol, resorcinol, pyrogallol, propionic acid, valeric acid and succinic acid.

(2) We have obtained experimental evidence in support of the theory that this phenomenon is caused by the adsorption of the organic solute at the glass-solution interface as well as at the vapor-solution interface.

(3) Contrary to the opinion of du Notty we have shown that the phenomenon may be observed and adequately studied by the capillary rise method. Several of the facts which we have found could hardly be observed in any dynamic method of measuring surface tension.

(4) We have observed, perhaps for the first time, that solutions of certain esters and alcohols show an increase in surface tension with time. With these solutions, after a rise to a maximum, the fresh surface formed by agitation displays the original minimum value, from which another rise will start at once. A careful study of such changes as they occur with solutions of ethyl acetate has been made.

(5) We have offered a plausible explanation of the phenomenon, and have obtained much experimental evidence in its support.

(6) We have demonstrated the necessity of using a closed capillarimeter in measuring the surface tensions of numerous solutions and have shown that rubber connections cannot be used.

(7) We have measured the surprisingly small quantity of solute necessary to produce extensive lowering of the surface tension in a new way, one of which may have some applications.

(8) We have suggested a method for estimating the rates of diffusion to and from surfaces, and for estimating the concentration at the surface of a meniscus.

(9) We have devised a method for estimating the degree of hydrolysis of a solution of an ester.

(10) In conclusion; we believe we have contributed in some slight measure, at least, to our knowledge of the possibilities and limitations of the capillary rise method of measuring surface tension.

THE CRYSTAL STRUCTURE OF POTASSIUM

BY E. POSNJAK

Introduction

Among the large number of substances which have at one time or another been X-rayed, the record for potassium is, in a way, a singular one. According to the record no regular diffraction of X-rays, but only a so-called general scattering is obtained at room temperature by the usual powder method. The first to investigate the crystal structure of the alkali metals was A. W. Hull.¹ He reports encountering considerable difficulties in obtaining X-ray diffractions from sodium and lithium and the failure to obtain any from potassium. The observation that no diffraction was obtained from samples made from freshly melted sodium and lithium and that even samples made from old stock produced a large amount of continuous scattering led him to believe that sodium and lithium were only partly crystalline and that the potassium must be completely amorphous. Later McKeehan² reinvestigated potassium. He found that if the potassium is cooled to -150° , weak reflections as from large crystals are obtained; however, he says that this "crystalline structure does not persist when the temperature is allowed to rise again to about 20° ."

The conclusion derived from X-ray experiments, that potassium must be amorphous at room temperature, is very surprising, as the fractured surface of potassium shows brilliant facets and well-defined crystals have been grown even from the molten metal³; and further, of course, because potassium has a definite and sharp melting and freezing point. It is not quite conceivable that an amorphous substance could possess such properties, and R. W. G. Wyckoff⁴ in discussing this case in his book on "The Structure of Crystals" tries to explain these conflicting facts by the assumption, not that potassium is an amorphous substance, but that the amplitudes of the thermal vibrations of potassium atoms at room temperature are so great as to "obliterate the crystalline diffraction maxima." We do not need, however, to go into the details of this discussion, as it will be shown below that the assumption is unnecessary. The reason for mentioning it is chiefly to call attention to the danger of drawing definite conclusions and of putting too much reliance on a few negative results of X-ray experimentation.

The present investigation grew out of experiments on non-crystalline substances, of which potassium was supposed to be one. Contrary to such statements, every sample of potassium that was X-rayed in this investigation

¹ Phys. Rev., 10, 661 (1917).

² Proc. Nat. Acad. Sci., 8, 254 (1922).

³ C. E. Long: J. Chem. Soc., 13, 122 (1860); F. Schroedler: Ann., 20, 2 (1836); A. Pleischl: J. prakt. Chem., 31, 45 (1844).

⁴ Wyckoff: "The Structure of Crystals," 372-373 (1924).

showed normal diffraction effects. In view of this, and for comparison results, a few preparations of sodium and one of lithium were made and X-rayed. These substances also in each case gave definite diffraction effects, which were in good agreement with previous determinations of their crystal structure, and only a short statement concerning these experiments will therefore be given below.

Experimental Part

Material and preparation of samples. Metallic potassium from two different sources was used in this work. The stock of one had been in this Laboratory for more than ten or fifteen years and had been originally obtained from the firm of Eimer and Amend. The other was specially obtained for the present experiments from the J. T. Baker Chemical Company (lot NS 52827). Their melting and their freezing points were determined approximately and found to lie close to 62° , which is very near the accepted value for potassium.

Owing to the original interest in potassium as a supposedly non-crystalline substance, Hull's observation, that the freshly melted or distilled alkali metals appeared to be in an amorphous condition, served to indicate the way of preparing such samples. After some trials, it was found that a thin capillary tube could readily be filled with potassium when the metal was in the molten condition. The following simple procedure was used. A Pyrex tube about 30 cm long and about 2 cm in diameter was sealed off at one end, and a side tube with a good stopcock was sealed on near the open end of the tube. Drawing out a piece of "Jena Geräte Glas" tubing partly into a thin capillary, and inserting the sealed-off end of this tube into a rubber stopper, the length of the capillary was adjusted so that when the rubber stopper with the drawn-out capillary was inserted into the open end of the Pyrex tube, the end of the capillary was about 2 or 3 mm above the bottom of the Pyrex tube. Pieces of potassium were cut free from crusts and were quickly placed in the tube by taking out the rubber stopper with the capillary projecting into the tube, which was then immediately put back and the whole evacuated by attaching the side tube with the glass stopcock to a pump. After the tube and the capillary inside of it were well evacuated, the pieces of potassium, which were all placed along the side of the tube, were gently heated to cause the metal to melt and to flow to the bottom of the tube. The capillary was then dipping directly into the molten metal. The oxide, which could not be prevented from forming during the cutting of the pieces of potassium and their insertion into the tube, usually stuck to the walls of the tube or floated on the surface of the metal. By suddenly letting a sufficient amount of nitrogen into the tube through the glass stopcock connection, some of the potassium which was about 15 to 20° above its melting point was forced into the capillary and almost immediately solidified there. After allowing the tube to cool off, the stopcock was opened to relieve the vacuum, and the rubber stopper with the capillary was taken out. A suitable length of the capillary filled with potassium, which was approximately 0.5 mm in

diameter, was then sealed off at both ends. This was done by very quick heating and drawing out of the glass, and required for its successful accomplishment a little practice, as overheating caused the metal to react with the glass. This rather detailed description of the preparation of the samples is given on account of the disagreement of the present findings with the former investigations, and because it is thought that the reason for the different findings must lie in the preparation of the sample of potassium.

The samples prepared in this way, on exposure to X-rays by the powder method, were found to give diffraction spots, some only a few while others produced a considerable number of spots. It was quite obvious that this was due to the size and number of crystals present in the sample. To increase the number and reduce the size of the crystalline particles, heat treatment was resorted to. The samples were heated in water about 20° above the melting point of potassium and then quickly quenched by placing them in a salt solution at about -18° . A picture of a sample treated in this way showed a large increase in the number of diffraction spots. However, it seemed probable that the rate at which crystals of potassium grew would make it very difficult to obtain by quenching a sufficiently fine-grained preparation and no special attempt in this direction was therefore made. Instead, the well-known method of rotating the sample was used and heat-treated preparations were attached to a motor, which rotated them around their axis at the rate of a revolution per minute during the exposure to X-rays. In this way satisfactory diffraction pictures were obtained.

The diffraction data from potassium and its crystal structure. The diffraction apparatus used was one made by the General Electric Company¹ in which the $K\alpha$ radiation of molybdenum is used and in which the distance between sample and photographic film is eight inches. The time of exposure was normal, approximately 250 m.a.h. Sodium chloride was used as usual for the standardization of the spacings.

Spacing measurements of the diffraction lines recorded on a photographic film are given in the first column of Table I. The estimated relative intensities of these lines and the squares of the sines of their angles of reflection are given in columns two and three of the table. It is well known that the ratios of the $\sin^2 \theta$ should give for a cubic crystal values of whole numbers, which are usually small. As will be seen in column four this is the case within the limits of the experimental errors. These whole numbers represent the sum of $(h^2+k^2+l^2)$ and serve to assign the indices of the planes producing the diffraction lines (columns five and six). In the last column of Table I, the resulting value of the length of the edge of the unit cube is given for each observed diffraction line.

Photographs were obtained from several other preparations and all gave practically identical results. The average values of the length of the edge of the unit cube for each preparation are given in Table II.

¹ W. P. Davey: Gen. Elect. Rev., 25, 565 (1922).

TABLE I
Powder photographic data from potassium.

| Spacing | Estimated intensity | $\sin^2\theta$ | Ratios of $\sin^2\theta$ | $h^2+k^2+l^2$ | Indices | a_0 |
|---------|---------------------|----------------|--------------------------|---------------|---------|-------|
| 3.770 | 10 | 0.00886 | 2.07 | 2 | 110(1) | 5.332 |
| 2.670 | 4 | .01768 | 4.05 | 4 | 100(2) | 5.340 |
| 2.170 | 6 | .02675 | 6.06 | 6 | 112(1) | 5.320 |
| 1.889 | 4 | .03530 | 8.00 | 8 | 110(2) | 5.336 |
| 1.677 | 3 | .0448 | 10.15 | 10 | 130(1) | 5.310 |
| 1.537 | 1 | .0533 | 12.07 | 12 | 111(2) | 5.325 |
| 1.428 | 2 | .0617 | 13.98 | 14 | 123(1) | 5.343 |

Average = 5.329 Å

TABLE II
Average value of a_0 from different samples.

| Film number | a_0 |
|-------------|---------|
| 135 | 5.335 Å |
| 145 | 5.334 |
| 170 | 5.329 |
| 175 | 5.333 |

Average $a_0 = 5.333 \pm 0.005$ Å.

While not definitely established, it is probable that potassium crystallizes in the cubic system. A careful determination of the density of the alkali metals has been made by T. W. Richards and T. N. Brink¹, giving for potassium at 20° the value of 0.862. Introducing this value in the usual equation $a_0^3 = mM/\rho$, where a_0^3 is the volume of the cube, m the number of atoms of potassium within the unit, M the mass of the potassium atom and ρ the density of potassium, we find that $m = 2.02$. This is within experimental error a whole number, as it should be. Accepting, conversely, that two atoms are associated with the unit cell of potassium, the density of potassium calculated by the above formula assumes the value 0.851, which is in good agreement with the direct determination.

The only possible cubic arrangement for two like atoms in the unit cell is the body-centered one, with the coordinates: 000; $\frac{1}{2} \frac{1}{2} \frac{1}{2}$. The characteristic structure factor of the body-centered cubic lattice requires that the sum of the indices must be an even number for reflection. As may be seen from Table I this requirement is fulfilled and no other reflections occur.

We may further use the semi-empirical formula²

$$I \propto (A^2 + B^2) \times (d/n)^{2.35} \times j$$

¹ J. Am. Chem. Soc., 29, 117 (1907).

² Wyckoff: "The Structure of Crystals," 201 (1924).

to calculate for the different planes the intensity of reflection expected for the body-centered arrangement and compare these values, reduced to the same basis, with the estimates of the relative intensity made directly. The results in both cases are always only a rough approximation but a general agreement between the observed and calculated values will be readily seen from Table III, confirming further the correctness of the body-centered cubic structure.

TABLE III
Comparison between the observed and calculated intensities from the different reflecting planes of potassium.

| Indices | Intensities | |
|---------|-------------|------------|
| | observed | calculated |
| 110 (1) | 10 | 10.0 |
| 100 (2) | 4 | 2.2 |
| 112 (1) | 6 | 5.5 |
| 110 (2) | 4 | 2.0 |
| 130 (1) | 3 | 3.0 |
| 111 (2) | 1 | 0.8 |
| 123 (1) | 2 | 4.1 |

Experiments with sodium and lithium. As mentioned above, a few samples of sodium and one of lithium were made and X-rayed in the same manner as were those of potassium. No difficulties were experienced in preparing samples of sodium, but lithium reacted very readily with the glass, probably owing primarily to its higher melting-point. After several attempts a sample of lithium was prepared, which, although it was not so good as those used with the other metals and although it produced considerable general blackening of the film, gave, however, four diffraction lines. In the former investigation of the structure of lithium by J. M. Bijvoet and A. Karssen¹ also only four diffraction lines were obtained and in view of the identical results it was not considered worth while to attempt preparing other samples. In complete agreement with earlier determinations, the length of the side of the unit cube for sodium was found to be 4.30 Å, and for lithium 3.51 Å.

Concerning general scattering from the alkali metals. Considerable stress has been laid on the general scattering obtained from the alkali metals, which was usually ascribed to the amorphous condition of the substance to a smaller or larger extent. The present experiments, while not carried far enough to find the direct cause of such scattering, strongly indicate that such an amorphous portion in all probability does not exist in the metal. Little if any general scattering was obtained from carefully prepared samples of potassium, and a comparison experiment showed that the amount was approximately the same as that produced by sodium chloride exposed in a similar glass capillary for the same length of time. The observations made seem to indicate that the general scattering is due rather to the formation of films produced by oxidation, moisture or the interaction of the alkali metals with the glass. Some samples of sodium which were probably overheated showed a slight

¹ Proc. Roy. Acad. Sci. Amsterdam, 23, 1365 (1921); Rec. Trav. chim., 42, 859 (1923).

discoloration and produced more of the general scattering than others, and the sample of lithium, which of course had to be heated considerably higher, produced accordingly a large amount of blackening on the film for approximately the same exposure.

McKeehan did not give any experimental data and it is therefore impossible to form a definite opinion in regard to the diffractions obtained by him from a sample of potassium kept at -150° during the exposure. However, the fact that nothing but general scattering was produced when the same sample was exposed at room temperature would, as a result of the present work, suggest that the weak diffraction obtained at -150° may possibly have resulted from the freezing out of some crystals of potassium hydroxide, which disappeared when the exposure was made at room temperature, owing to the melting of the crystals and formation of a liquid film.

Summary

Contrary to former statements, normal diffraction effects are obtained from potassium at room temperature by the powder method.

The reason for obtaining only a general scattering and no definite diffraction in former experiments is thought to be the formation of films on the sample of potassium by moisture, by oxidation, or by interaction of the potassium with the glass.

The method used for the preparation of samples of potassium is described.

The available data indicate that potassium crystallizes in the body-centered cubic lattice. The length of the edge of the unit cube containing two atoms of potassium is $5.333 \pm 0.005 \text{ \AA}$. The calculated density is 0.851.

The lengths of the edges of the unit cubes of sodium and lithium were re-determined and, in agreement with earlier determinations, the value obtained for the former was 4.30 \AA and for the latter 3.51 \AA .

*Geophysical Laboratory,
Carnegie Institution of Washington,
November, 1927.*

22-15

THE HEATS OF ADSORPTION OF CERTAIN ORGANIC VAPORS ON CHARCOAL AT 25°

BY J. N. PEARCE AND LLOYD MCKINLEY

While the adsorptive power of solid porous bodies for gases is a phenomenon that has challenged the attention of many investigators during the last century, the amount of quantitative data which has accumulated dealing with the heat effect accompanying adsorption is rather limited and is confined, for the most part, to the results of comparatively recent investigations. Although the thermal effect of adsorption had been observed by Mitscherlich¹ in 1843, Favre,² using a mercury calorimeter, was the first to make a quantitative measurement of the heats of adsorption of a number of gases on charcoal and of hydrogen on platinum. By the use of an ice-calorimeter Chappuis³ measured the heats of adsorption of sulphur dioxide, ammonia and carbon dioxide on charcoal, meerschaum, platinum black and asbestos. Dewar⁴, with the aid of a liquid-air calorimeter, measured the heats of adsorption of the permanent gases on charcoal at the temperature of liquid air. Homfray⁵ has shown that a certain thermodynamical formula is applicable for calculating the molecular heat of adsorption of carbon dioxide on charcoal. Using an ice-calorimeter, Titoff⁶ obtained consistent values for the thermal effect of adsorption of nitrogen, ammonia and carbon dioxide on charcoal. The heats of adsorption of sulphur dioxide and ammonia on silica gel have been measured by Patrick and Greider.⁷ Lamb and Coolidge⁸ have obtained values for the heats of adsorption of eleven organic vapors on charcoal. Whitehouse⁹ has measured the heat effect produced in the adsorption of carbon dioxide, methane and nitrogen on coals and charcoal. All of these investigators, with the exception of Favre, Homfray and Dewar, have made use of the ice-calorimeter. Beebe and Taylor,¹⁰ and Dew and Taylor,¹¹ have recently measured the heats of adsorption of hydrogen and ammonia, respectively, on copper and nickel by a rapid method in which the catalyst tube, itself, serves as the calorimeter. They do not, however, claim an accuracy better than 10 percent.

As can be noted from the above review of the literature, the majority of the measurements of the heats of adsorption, thus far, have been made at 0°.

¹ Mitscherlich: *Ann. Chim. Phys.*, (3), 7, 18 (1843).

² Favre: *Ann. Chim. Phys.*, (5) 1, 209 (1874).

³ Chappuis: *Ann. Chim. Phys.*, (2) 19, 21 (1883).

⁴ Dewar: *Proc. Roy. Soc.*, 74, 122 (1904).

⁵ Homfray: *Z. physik. Chem.*, 74, 129 (1910).

⁶ Titoff: *Z. physik. Chem.*, 74, 641 (1910).

⁷ Patrick and Greider: *J. Phys. Chem.*, 29, 1031 (1925).

⁸ Lamb and Coolidge: *J. Am. Chem. Soc.*, 42, 1146 (1920).

⁹ Whitehouse: *J. Soc. Chem. Ind.*, 45, 13 (1926).

¹⁰ Beebe and Taylor: *J. Am. Chem. Soc.*, 26, 43 (1924).

¹¹ Dew and Taylor: *J. Phys. Chem.*, 31, 277 (1927).

Popular as the ice-calorimeter is, it does not permit an investigation at other temperatures. Except for the more difficultly liquefiable gases and vapors, most vapors condense to the liquid state at 0° . This, and the fact that in adsorption there may be a "forced" condensation, does not permit us to separate the thermal effects of the two kinds of condensation. Furthermore, until we are in possession of means of measuring the heat of adsorption at different temperatures, we shall not be able to determine experimentally the effect of temperature upon the heat of adsorption.

The purpose of this investigation was to devise and apply a calorimetric method for measuring the heats of adsorption at any desired temperature. By using higher temperatures we hope later to overcome certain difficulties which arise when working at the temperature of melting ice. Objectionable condensation effects will be avoided, and higher equilibrium pressures can be attained. Although we have not avoided condensation effects by working at 25° , we have, nevertheless, chosen it as our working temperature in this preliminary work. Measurements have been made purposely on some of the vapors studied by Lamb and Coolidge at 0° . In this way we hoped, by comparison, to show the accuracy attainable by the method.

Materials

The charcoal used in this investigation was taken from a large supply which has served as the basis of an extensive study of adsorption in this laboratory. It was prepared for us by the Carbide and Carbon Chemicals Corporation under the direction of Dr. N. K. Chaney. It is a coconut shell charcoal which has been activated by steam, treated with acid to remove mineral matter, and then washed until acid-free. The size of the granules used range from 12 to 20 mesh. Previous determinations showed the ash-content to be 0.28 percent by weight.

The loss in weight on outgassing and the density of the charcoal have been determined in an earlier work.¹² For the former, a weighed sample of the charcoal was evacuated under identical conditions employed in the regular adsorption experiments. When the pressure had remained constant at about 0.0001 mm. for several hours the tube was sealed off and weighed. The mean of three very concordant determinations showed a 2.50 percent loss in weight on outgassing; this correction was applied in calculating the actual weight of the adsorbent used. The density of the charcoal was determined by the method of Cude and Hulett,¹³ using water as the immersion liquid and disregarding the drift after the first few hours. The mean of four determinations, 1.800, was taken as the density and was used in correcting for the "dead space."

The liquids, whose vapors were studied, were purified carefully by accepted methods,¹⁴ and then fractionated. Only the middle portion of each fractionation was collected. These liquids were prepared immediately before using.

¹² Pearce and Knudson: Proc. Iowa Acad. Sciences, (1927).

¹³ Cude and Hulett: J. Am. Chem. Soc., 42, 391 (1920).

¹⁴ Mathews: J. Am. Chem. Soc., 48, 562 (1926).

Apparatus

The apparatus is shown in Figs. 1 and 1a. It combines the advantages of recently improved adsorption apparatus with those of a calorimeter which may be used at any temperature. The net result is an apparatus more potential in possibilities than any, hitherto used in measuring the heats of adsorption.

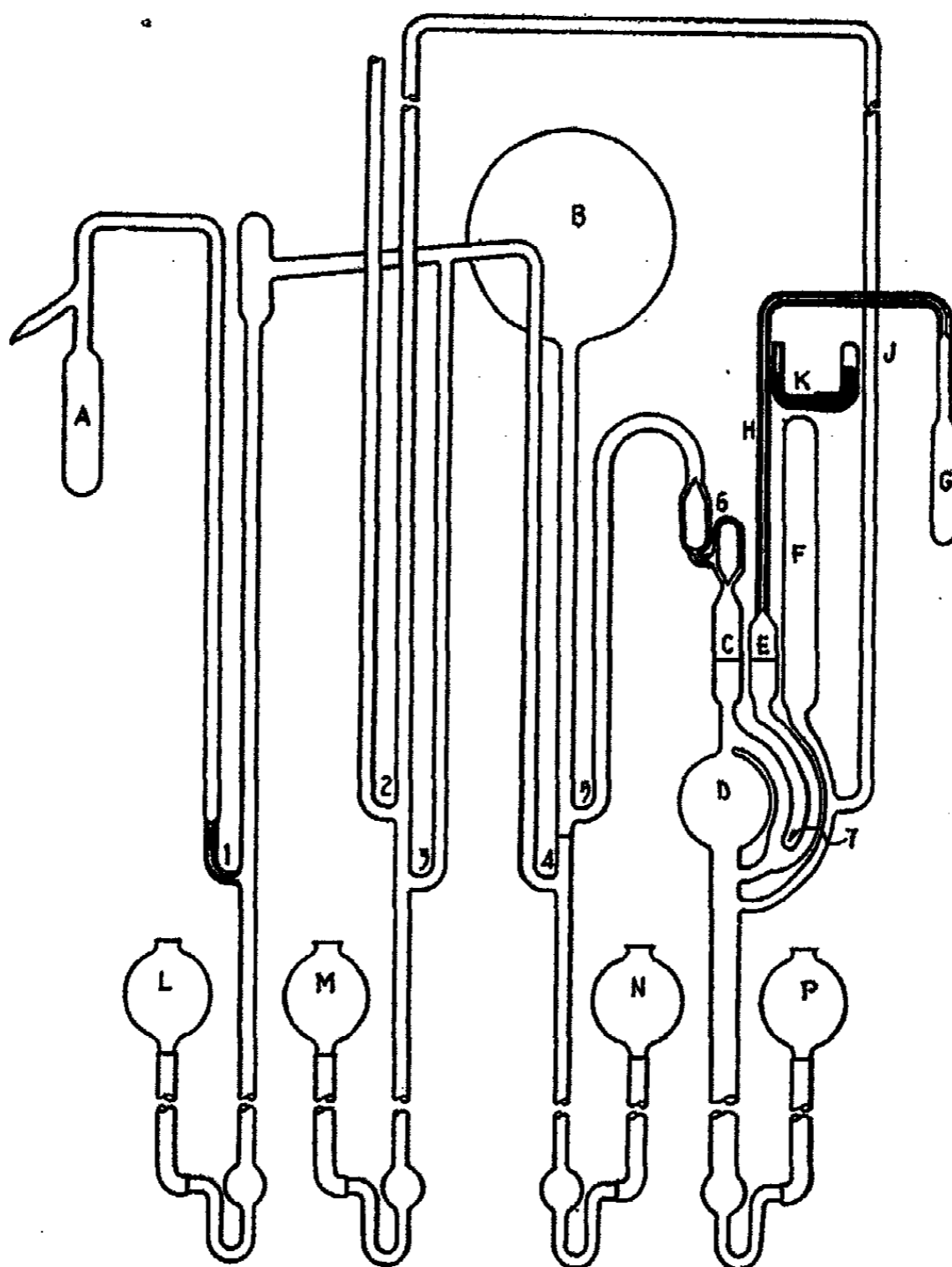


FIG. 1

Adsorption Apparatus.—The adsorption apparatus consists of one continuous line of Pyrex tubing and flasks, with no stopcocks or rubber connections above the mercury levels; it is, essentially, in design and principle, the same as that used by Coolidge.¹⁵ For the sake of brevity, a detailed explanation

¹⁵ Coolidge: *J. Am. Chem. Soc.*, 46, 596 (1924).

of the various parts is omitted. A detailed description of the apparatus and its operation is given in the original paper.

Calorimeter.—The calorimeter, R, is a wide-mouth Dewar flask, fitted with a cork stopper with openings for the charcoal bulb, G, the spiral rotary stirrer, P, one arm of the thermocouple, Q, and a special low lag heating coil, N.

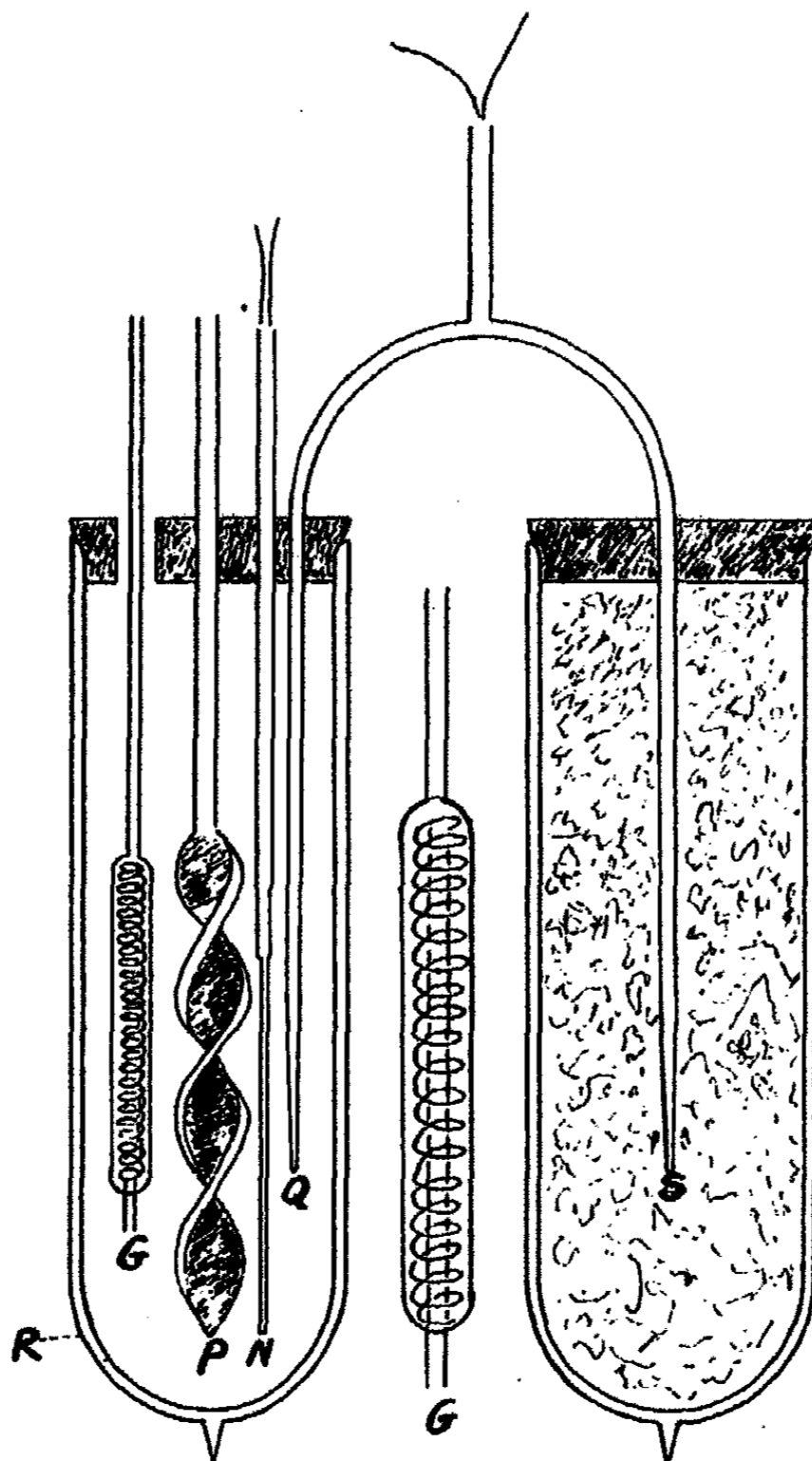


FIG. 1a

The charcoal bulb of "702 P" Pyrex glass, Fig. 1a, G, contains a spiral and a straight piece of tungsten wire, both sealed into the bottom of the bulb so that about 2 cms. protrude. The wires within the bulb are so arranged that the distance between the adjacent wires does not exceed 3 mm. In this way the heat liberated in the adsorption process is quickly conducted from the charcoal surface to the calorimeter liquid.

Constant Temperature Bath.—The complete apparatus with the exception of the bulb, A, is inclosed in a double-walled, electrically heated and electrically controlled air-bath mounted on a heavy table. Efficient stirring is obtained by a system of high-speed fans which maintain a continuous and rapid circulation of air through the bath, over the cooling coils at the top, then down between the walls at the sides, and finally past the low lag heating coils into the bottom of the bath. This efficient circulation of the air, together with a 5-foot upright multiple-tube mercury regulator in series with a Bunnell relay, enabled us to control the temperature of the bath to within $\pm 0.05^\circ$. At the front and back are large double doors which provide, not only a non-conducting air space, but also a ready means of accessibility to the apparatus when in need of alteration or repairs. The glass doors at the front permitted readings of the bath temperature and of the vapor pressures by means of a cathetometer placed outside. Ideal working conditions were realized by means of a special precision system of mercury controlling devices operated from a panel of convenient switches on the front of the table.

The volume of the reservoir, B, together with the connecting tube to the mark between valves 4 and 5, and thence to the mark on C, was determined from its water capacity before the apparatus was assembled. The volume of the charcoal bulb, G, plus the capillary tube to the mark on E, was likewise calibrated with mercury before assembling.

Thermo-element.—The 25-junction copper-constantan thermo-element was made in strict accord with the specifications given by White.¹⁶ The element was accurately standardized against a certified thermo-element at three points, namely, the transition points of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, and liquid air. The salts were carefully purified according to the methods of Richards and Wrede,¹⁷ and of Richards and Wells,¹⁸ respectively. The reference ice bath consisted of a large Dewar flask containing pure ice moistened with conductivity water. Since the thermal measurements made in this work were at 25° , we have calculated the potentials corresponding to 25° and 26° . They were found to be $22856\mu\text{v}$ and $23802\mu\text{v}$, respectively; the difference corresponds to 0.0010559° per $1\mu\text{v}$.

Thermal Capacity of the Calorimeter.—The calibration of the calorimeter system with water as the calorimeter liquid was made electrically by passing an accurately known quantity of electricity through a heating coil of known resistance. This coil consisted of about 100 cms. of No. 36 constantan wire wound around a thin mica strip. It was insulated by two similar strips of mica and inclosed in a close fitting copper case. Two heavy insulated copper leads pass from the case, proper, through a short metal tube that is cemented to a glass tube, which serves as a handle and as a heat insulator. The metallic parts of the receptacle, which is made air tight by soldering, is heavily plated with silver and polished. The resistance is 52 ohms, and in operation delivers about 3 watts.

¹⁶ White, J. Am. Chem. Soc., 36, 2292 (1914).

¹⁷ Richards and Wrede, Z. physik. Chem., 61, 313 (1907).

¹⁸ Richards and Wells, Z. physik. Chem., 43, 465 (1903).

Method of Calibration.—The heating coil was connected in series with a standard 1-ohm resistance, a laboratory slide rheostat and a very sensitive Bradleystat. A battery of seven large storage cells supplied the current. Across the standard ohm and the heating element were connected a Leeds and Northrup, "Type K," potentiometer and a volt-box, respectively. With this arrangement, the potentiometer reads directly in amperes, whereas the volt-box in conjunction with a student potentiometer permits the reading of the volts. With the potentiometer set to read the amount of current chosen to flow through the system, the rheostat was adjusted so that a slight manipulation of the Bradleystat enables the operator to maintain a current whose variations at any instant never exceed 1 part in 1000. A sensitive galvanometer indicated the deviations which can be instantly corrected. The voltage drop across the heating coil was read at intervals of one minute, and was found to be practically constant. When the voltage did actually vary, the average value during the interval was calculated and used. The time of passage of the current was measured by means of a stop watch, reading to 0.2 sec.

The increase in temperature during a calibration, although small, corresponded to an increment of approximately 2000 μv . Since the galvanometer was responsive to deviations of 1 μv ., the possible error in this measurement was not greater than 0.1 percent. Radiation, though perceptible, was measurable. The magnitude of the radiation was greatly reduced by starting the calibration at a calorimeter temperature that was as far below, as the final temperature was above, that of the constant temperature bath.

The results of two determinations of the thermal capacity of the calorimeter and its fixtures were 51.26 cal. and 51.42 cal., with a deviation from the mean, 51.34 cal., of less than 0.2 percent. The value of 51.34 cal. was accordingly accepted as the thermal capacity of the calorimeter and was used in all subsequent calculations.

Specific Heat of "Finol."—Following the same procedure as outlined for water, we obtained the thermal capacity of the calorimeter system and liquid when charged with an accurately known weight of a light oil, which is sold under the trade name of "Finol." With 300 cc. of this oil in the calorimeter, the total heat capacity is only about 165 cal., an amount which is less than one-half that with an equal volume of water as the liquid. Three different determinations of the specific heat of the oil, in calories, over the range from 25° to 28°, gave the values 0.4500, 0.4492 and 0.4512, respectively, or a mean specific heat of 0.4501 cal.

Sensitivity of Calorimeter

The thermal capacity of the calorimeter and liquid is equal to the thermal capacity of the calorimeter, (51.34), plus the product of the weight of the oil times its specific heat, 0.4501 cal. For the average weight of oil used, this amounts to 165 cal. Since the thermo-couple used was sensitive to 0.001°, the calorimeter system responds to a heat transfer of 0.17 cal. In using the ice calorimeter for their measurements, Lamb and Coolidge state that on their

scale a millimeter movement of the mercury thread, during the change of state from ice to water, corresponds to 0.589 cal. Hence the resulting sensitivity of the ice calorimeter is three times that of our calorimeter, if the displacement of the mercury thread can be read to 0.1 mm. The results of our work show, however, that this difference in sensitivity is not appreciable.

Experimental Method

The charcoal bulb, first weighed empty and then full of charcoal, is sealed into position, inclosed in an electric furnace at 550°, and evacuated until the McLeod gage, (not shown in Fig.), indicates a pressure of 0.0001 mm., or less. All of the mercury levels are lowered so that the whole system is evacuated at the same time. Mercury well, L, is now raised, closing valve 1, the pumping is discontinued and the furnace is allowed to cool. The procedure involved in charging A with liquid and B with vapor, as well as that involved in transferring the vapor to the charcoal, if not evident to the reader, can be found in the paper by Coolidge,¹⁵ who worked with a similar apparatus. An additional feature is a reservoir used when the transfer of large volumes of vapor is required to produce high equilibrium pressures. This consists of a mercury well and bulb (not shown), but attached to the capillary, H.

The calorimeter is charged with a weighed amount of oil, initially at or very near the temperature of the bath, and is allowed to stand with intermittent stirring until a constant reading of the thermo-element is obtained. When thermal equilibrium is attained and the cathetometer pressure readings become constant, a sample of the vapor is transferred to the charcoal by means of the pump, D. After the admission of the vapor to the charcoal, the liquid is stirred intermittently for periods of one to three minutes. During this time the thermo-element potentials are read at one minute intervals until the potential attains a constant value, or until a constant rate of radiation is indicated. Pressure readings are then taken of the vapor remaining in the reservoir, and of the vapor in equilibrium with the charcoal. Once the equilibrium is established and the data recorded, a new sample of vapor is admitted. With each admission of vapor, there are recorded the potential increments in microvolts, the corresponding drop in the presence of the vapor in B, and the successively increasing equilibrium pressures over the charcoal. When the equilibrium pressure has attained a value just short of that at saturation a series of adsorption experiments, or "run," is assumed to be completed.

Calculation of Results

The results are expressed in small calories and cc. of gas (N.T.P.) per gram of gas-free charcoal. The vapor pressures were corrected for altitude and temperature, and the gas laws were applied in calculating the volume of the vapor. The complete calculations of an experiment are given below.

| | |
|----------------------------------------|------------|
| Weight of charcoal and glass bulb..... | 28.6705 g. |
| Weight of bulb..... | 25.5844 g. |
| Weight of charcoal..... | 3.0861 g. |

| | |
|----------------------------------------------------------------|------------|
| Corrected weight of charcoal ¹³ | 3.0089 g. |
| Volume of total reservoir system (N.T.P.)..... | 2203.6 cc. |
| Pressure in B before adsorption..... | 9.775 cm. |
| Pressure in B after adsorption..... | 8.755 cm. |
| Drop in pressure..... | 1.020 cm. |
| Correction for temperature and altitude..... | 0.005 cm. |
| Corrected pressure drop in B..... | 1.015 cm. |
| Gas removed (per g. of char.) for 1 cm. drop in pressure:..... | |

$$\frac{2203.6 \times 273}{76 \times 298 \times 3.0089} = 8.828 \text{ cc.}$$

| | |
|-----------------------------------------------------|------------|
| For 1.015 cm. drop the cc./g. removed is..... | 8.96 cc. |
| Pressure in charcoal bulb at equilibrium..... | 0.00 cm. |
| Volume of bulb and tubing to calibration marks..... | 14.900 cc. |
| Volume of charcoal: 3.0089 + 1.800..... | 1.671 cc. |
| Volume of "dead space"..... | 12.229 cc. |

$$\frac{13.229 \times 273}{76 \times 298 \times 3.0089} = 0.053 \text{ cc./g.}$$

| | |
|-----------------------------------------------------|----------------|
| Gas removed but not adsorbed..... | 0.00 cc./g. |
| Gas adsorbed "x"..... | 8.96 cc./g. |
| Initial reading of thermocouple at 7.46 P.M..... | 22874 μ V. |
| Time required to introduce vapor: 7.46 to 7.52..... | 6 min. |
| Stirrer started at 7.52 (60 R.P.M.) | |

| Time | Thermocouple reading |
|---------------------------------------------------------|----------------------|
| 7.54 | 22941 μ V. |
| 7.55 | 22958 μ V. |
| 7.56 | 22965 μ V. |
| Rate of stirring decreased (30 R.P.M.) | |
| 7.57 | 22970 μ V. |
| 7.58 | 22975 μ V. |
| Stirrer stopped. | |
| 8.00 | 22979 μ V. |
| (At this time pressure readings were taken) | |
| 8.13 | 22996 μ V. |
| Stirrer operated 1 min. | |
| 8.15 | 22990 μ V. |
| 8.16 | 22990 μ V. |
| 8.19 | 22990 μ V. |
| Final reading of the thermocouple..... | 22990 μ V. |
| Increase in microvolts..... | 116 μ V. |
| Weight of oil in calorimeter..... | 252.66 g. |
| Cal./g. evolved corresponding to increase of 1 μ V: | |

$$\frac{(252.66 \times 0.4501) - 51.34}{947 \times 3.0089} = 0.057927 \text{ cal./g./}\mu\text{v.}$$

Total heat evolved per gram of charcoal, "h": $116 \times 0.057927 = 6.72 \text{ cal./g.}$

The results of each experiment, namely, the drop in pressure and the heat evolved are added to those of the preceding experiments of the same run, thus giving the total heat evolved, h , and the total drop in pressure in B, during the adsorption of the vapor. This change in pressure enables us to calculate the total gas volume, x , adsorbed by the charcoal.

Results

The results of the study of the heats of adsorption of nine vapors on charcoal are recorded in the following Tables. The first column in each gives the equilibrium pressure observed at the time when the final calorimeter reading

TABLE I
The Heat of Adsorption of Acetone Vapor at Charcoal at 25°

| P cm. | X cc./g. | ΔE $\mu\text{v.}$ | Δh cal./g. | Σh cal./g. | Σh cal./g. | Δ cal./g. |
|---------------|-------------------------|------------------------------|-----------------------|-----------------------|-----------------------|---------------------|
| — | 6.44 | 77 | 4.59 | 4.59 | 4.55 | -0.04 |
| — | 15.90 | 111 | 6.62 | 11.21 | 10.78 | -0.63 |
| — | 29.45 | 137 | 8.15 | 19.36 | 19.40 | +0.04 |
| 0.110 | 47.93 | 194 | 11.53 | 30.89 | 30.87 | -0.02 |
| 0.245 | 64.76 | 202 | 12.01 | 42.90 | 41.13 | -0.77 |
| 4.085 | 99.87 | 330 | 19.62 | 62.52 | 62.21 | -0.30 |
| 13.024 | 109.28 | 90 | 5.35 | 67.87 | 67.72 | -0.15 |
| Fresh sample. | $h = 0.7713 x^{0.0534}$ | | | | | |

TABLE II
The Heat of Adsorption of Ether Vapor at Charcoal at 25°

| P cm. | X cc./g. | ΔE $\mu\text{v.}$ | Δh cal./g. | Σh_0 cal./g. | Σh_0 cal./g. | Δ cal./g. |
|-----------------------------|-------------------------|------------------------------|-----------------------|-------------------------|-------------------------|---------------------|
| — | 11.72 | 155 | 9.14 | 9.14 | 9.25 | +0.11 |
| — | 28.39 | 197 | 11.61 | 20.75 | 20.67 | -0.08 |
| — | 45.89 | 209 | 12.32 | 33.07 | 32.40 | -0.67 |
| 1.365 | 65.83 | 210 | 12.34 | 45.41 | 45.41 | 0.00 |
| 35.020 | 70.72 | 108 | 6.35 | 51.76 | 53.68 | (+1.92) |
| — | 8.39 | 108 | 6.36 | 6.36 | 6.61 | +0.25 |
| — | 24.26 | 193 | 11.49 | 17.85 | 17.85 | 0.00 |
| — | 39.81 | 186 | 10.96 | 28.81 | 28.37 | -0.44 |
| — | 55.36 | 161 | 9.48 | 38.29 | 38.62 | +0.33 |
| 4.185 | 66.99 | 143 | 8.42 | 46.71 | 47.44 | +0.73 |
| 36.718 | 78.00 | 61 | 3.59 | 50.30 | 53.22 | (+2.92) |
| Used previously on acetone. | $h = 0.9044 x^{0.0353}$ | | | | | |

TABLE III
The Heat of Adsorption of Carbon Disulphide Vapor by Charcoal at 25°

| P cm. | X cc./g. | ΔE $\mu v.$ | Δh cal./g. | Σh_0 cal./g. | Σh_c cal./g. | Δ cal./g. |
|----------|-------------|------------------------|-----------------------|-------------------------|-------------------------|---------------------|
| — | 3.73 | 50 | 2.98 | 2.94 | 2.61 | -0.33 |
| — | 18.81 | 150 | 8.93 | 11.78 | 11.38 | -0.40 |
| — | 32.84 | 131 | 7.80 | 19.49 | 18.92 | -0.57 |
| — | 46.43 | 117 | 6.97 | 26.33 | 25.94 | -0.39 |
| 0.475 | 59.57 | 102 | 6.07 | 32.39 | 32.55 | +0.16 |
| 0.860 | 77.52 | 147 | 8.73 | 41.04 | 41.35 | +0.31 |
| 5.952 | 114.83 | 324 | 19.29 | 60.13 | 59.18 | -0.95 |
| — | 7.50 | 82 | 4.82 | 4.82 | 4.93 | +0.11 |
| — | 20.56 | 128 | 7.53 | 12.35 | 12.35 | 0.00 |
| — | 31.78 | 99 | 5.82 | 18.17 | 18.36 | +0.19 |
| — | 42.27 | 84 | 4.94 | 23.11 | 23.81 | +0.70 |
| — | 62.70 | 179 | 10.53 | 33.64 | 34.10 | +0.46 |
| 0.630 | 84.29 | 183 | 10.77 | 44.41 | 44.65 | +0.24 |
| 1.742 | 106.08 | 181 | 10.65 | 55.06 | 55.06 | 0.00 |
| 21.145 | 130.45 | 184 | 10.82 | 65.88 | 66.47 | +0.59 |
| — | 11.67 | 123 | 7.24 | 7.24 | 7.37 | +0.13 |
| — | 30.56 | 187 | 11.01 | 18.25 | 17.72 | -0.53 |
| — | 55.90 | 221 | 13.02 | 31.27 | 30.71 | -0.56 |
| — | 81.28 | 204 | 12.02 | 43.39 | 43.19 | -0.20 |
| 1.135 | 102.75 | 174 | 10.25 | 53.54 | 53.48 | -0.06 |
| 20.006 | 128.27 | 189 | 11.13 | 64.67 | 65.46 | -0.79 |

Use previously in Expts. I and II. $h = 0.7861 x^{0.911}$

TABLE IV
The Heat of Adsorption of Benzene Vapor by Charcoal at 25°

| P cm. | X cc./g. | ΔE $\mu v.$ | Δh cal./g. | Σh_0 cal./g. | Σh_c cal./g. | Δ cal./g. |
|----------|-------------|------------------------|-----------------------|-------------------------|-------------------------|---------------------|
| — | 14.00 | 181 | 10.67 | 10.67 | 10.34 | -0.33 |
| — | 27.30 | 152 | 8.96 | 19.63 | 19.60 | -0.03 |
| — | 46.52 | 215 | 12.67 | 32.30 | 32.64 | +0.34 |
| — | 66.39 | 217 | 12.79 | 45.09 | 45.87 | +0.78 |
| — | 79.22 | 134 | 7.90 | 52.99 | 54.32 | +1.38 |
| 6.065 | 87.29 | 85 | 5.01 | 58.00 | 59.61 | +1.61 |
| — | 12.39 | 153 | 9.00 | 9.00 | 9.23 | +0.23 |
| — | 20.55 | 109 | 6.41 | 15.41 | 14.93 | -0.48 |
| — | 47.72 | 310 | 18.24 | 33.65 | 33.44 | -0.21 |
| — | 59.43 | 138 | 8.12 | 41.77 | 41.26 | -0.51 |
| — | 71.54 | 127 | 7.47 | 49.24 | 49.28 | +0.04 |
| 2.000 | 80.72 | 100 | 5.88 | 55.12 | 55.30 | +0.18 |
| 5.798 | 85.39 | 62 | 3.65 | 58.77 | | |

$$h = 0.828 x^{0.9560}$$

Used previously in expts. I, II and III.

was made. The second column gives the volume of gas in cc. (N.T.P.) adsorbed by 1 g. of gas-free charcoal. In the third are placed the increase in the thermocouple reading, in μv , accompanying the transfer of the vapor. These readings, converted to calories, Δh , are listed in the fourth column. The fifth contains the summation, Σh , of the heat effects of the previous additions of the same series. In the sixth are placed the values of Σh calculated by means of the exponential formula, placed at the bottom of the table. The previous history of the sample is also given below the results for each liquid.

TABLE V
The Heat of Adsorption of Ethyl Chloride Vapor by Charcoal at 25°

| P cm. | X cc./g. | ΔE μv . | Δh cal./g. | Σh_0 cal./g. | Σh_e cal./g. | Δ cal./g. |
|----------|-------------|-------------------------------|-----------------------|-------------------------|-------------------------|---------------------|
| — | 7.00 | 65 | 3.82 | 3.82 | 3.61 | -0.21 |
| — | 23.37 | 147 | 8.65 | 12.47 | 12.46 | -0.01 |
| — | 40.39 | 142 | 8.35 | 20.82 | 21.68 | +0.68 |
| 1.455 | 63.78 | 187 | 11.00 | 31.82 | 33.00 | +1.18 |
| 4.300 | 81.80 | 150 | 8.82 | 40.64 | 42.01 | +1.33 |
| 22.345 | 99.49 | 172 | 10.12 | 50.76 | 50.80 | +0.04 |
| — | 8.13 | 70 | 4.13 | 4.13 | 4.75 | +0.62 |
| — | 18.09 | 100 | 5.90 | 10.03 | 9.72 | +0.31 |
| — | 27.12 | 70 | 4.13 | 14.16 | 14.40 | +0.24 |
| — | 43.97 | 175 | 10.33 | 24.49 | 23.00 | -1.49 |
| 1.820 | 62.67 | 138 | 8.14 | 32.63 | 32.59 | -0.04 |
| 5.569 | 82.09 | 164 | 9.68 | 42.31 | 42.15 | -0.16 |

$$h = 0.5862 x^{0.9700}$$

Used previously in expts. I, II, III and IV.

TABLE VI
The Heat of Adsorption of Methyl Alcohol Vapor by Charcoal at 25°

| P cm. | X cc./g. | ΔE μv . | Δh cal./g. | Σh_0 cal./g. | Σh_e cal./g. | Δ cal./g. |
|----------|-------------|-------------------------------|-----------------------|-------------------------|-------------------------|---------------------|
| — | 15.32 | 180 | 10.43 | 10.43 | 10.49 | +0.06 |
| — | 29.74 | 155 | 8.98 | 19.41 | 19.20 | -0.21 |
| — | 44.11 | 139 | 8.05 | 27.46 | 27.50 | +0.04 |
| — | 63.75 | 191 | 11.06 | 38.52 | 38.46 | -0.06 |
| 0.840 | 85.50 | 198 | 11.47 | 49.99 | 50.26 | +0.27 |
| — | 8.96 | 116 | 6.72 | 6.72 | 6.44 | -0.28 |
| — | 23.42 | 150 | 8.69 | 15.41 | 15.45 | +0.04 |
| — | 33.13 | 85 | 4.98 | 20.39 | 21.19 | +0.80 |
| — | 48.41 | 144 | 8.34 | 28.73 | 29.93 | +1.20 |
| 0.485 | 74.65 | 254 | 14.71 | 43.44 | 44.42 | +0.98 |
| 0.725 | 98.80 | 217 | 12.57 | 56.01 | 57.33 | +1.32 |
| 1.430 | 126.41 | 302 | 17.46 | 73.47 | 71.77 | -1.70 |
| 4.135 | 158.03 | 253 | 14.62 | 88.09 | 87.96 | -0.13 |

Fresh sample. $h = 0.873 x^{0.9111}$

TABLE VII
The Heat of Adsorption of Chloroform by Charcoal at 25°

| P cm. | X cc./g. | ΔE $\mu v.$ | Δh cal./g. | Σh_0 cal./g. | Σh_c cal./g. | Δ cal./g. |
|----------|-------------|------------------------|-----------------------|-------------------------|-------------------------|---------------------|
| — | 9.40 | 117 | 6.76 | 6.76 | 6.74 | -0.02 |
| — | 20.83 | 133 | 7.69 | 14.45 | 14.18 | -0.27 |
| — | 34.84 | 152 | 8.79 | 23.24 | 22.94 | -0.30 |
| — | 56.41 | 218 | 12.60 | 35.84 | 36.00 | +0.16 |
| 0.465 | 74.80 | 186 | 10.75 | 46.59 | 46.87 | +0.28 |
| 12.382 | 94.45 | 175 | 10.12 | 56.71 | 58.30 | +1.59 |
| — | 12.40 | 151 | 8.73 | 8.73 | 8.73 | 0.00 |
| — | 31.63 | 219 | 12.66 | 21.39 | 20.96 | -0.43 |
| — | 47.63 | 161 | 9.31 | 30.70 | 30.73 | +0.03 |
| — | 67.30 | 193 | 11.16 | 41.86 | 42.37 | +0.51 |
| 2.702 | 81.23 | 141 | 8.15 | 50.01 | 50.63 | +0.62 |
| 13.188 | 90.82 | 41 | 4.97 | 54.98 | 56.20 | +1.23 |

Previously used with methyl alcohol. $h = 0.8295 x^{0.935}$

TABLE VIII
The Heat of Adsorption of Carbon Tetrachloride Vapor by Charcoal at 25°

| P cm. | X cc./g. | ΔE $\mu v.$ | Δh cal./g. | Σh_0 cal./g. | Σh_c cal./g. | Δ cal./g. |
|----------|-------------|------------------------|-----------------------|-------------------------|-------------------------|---------------------|
| — | 9.44 | 136 | 7.88 | 7.88 | 7.76 | -0.12 |
| — | 21.58 | 148 | 8.57 | 16.45 | 16.41 | -0.04 |
| — | 32.95 | 128 | 7.41 | 23.86 | 23.80 | -0.06 |
| — | 42.35 | 104 | 6.02 | 29.88 | 29.67 | -0.21 |
| 5.982 | 53.23 | 117 | 6.78 | 36.66 | 36.27 | -0.39 |
| 9.496 | 57.67 | 41 | 2.37 | 39.03 | 38.91 | +0.12 |
| — | 3.44 | 55 | 3.18 | 3.18 | 3.27 | +0.09 |
| — | 11.07 | 100 | 5.79 | 8.97 | 9.11 | +0.14 |
| — | 18.63 | 89 | 5.15 | 14.12 | 14.43 | +0.31 |
| 0.215 | 28.11 | 99 | 5.73 | 19.85 | 20.70 | +0.85 |
| 0.285 | 36.18 | 98 | 5.67 | 25.52 | 25.84 | +0.32 |
| 5.425 | 47.59 | 115 | 6.65 | 32.17 | 32.87 | +0.70 |

Used in expts. VI and VII. $h = 1.107 x^{0.878}$.

TABLE IX
The Heat of Adsorption of Propyl Chloride Vapor by Charcoal at 25°

| P cm. | X cc./g. | ΔE $\mu v.$ | Δh cal./g. | Σh_0 cal./g. | Σh_c cal./g. | Δ cal./g. |
|----------|-------------|------------------------|-----------------------|-------------------------|-------------------------|---------------------|
| — | 8.39 | 112 | 6.48 | 6.48 | 6.56 | +0.08 |
| — | 24.65 | 188 | 10.88 | 17.36 | 17.52 | +0.16 |
| 0.190 | 37.99 | 151 | 8.74 | 26.10 | 25.99 | -0.11 |
| 0.590 | 54.54 | 180 | 10.41 | 36.51 | 36.15 | -0.36 |
| 5.509 | 66.10 | 115 | 6.65 | 43.16 | 43.06 | -0.10 |
| 34.954 | 77.98 | 98 | 5.67 | 48.83 | 50.07 | +1.24 |

Used in expts. VI, VII and VIII. $h = 0.9441 x^{0.9915}$.

If the observed values of X and h are plotted, we obtain curves which are slightly concave toward the X-axis. Fig. 2 shows the curves for all of the vapors drawn from a common origin. In order to prevent overlapping, a plot is made in which the origin is displaced one square with respect to the

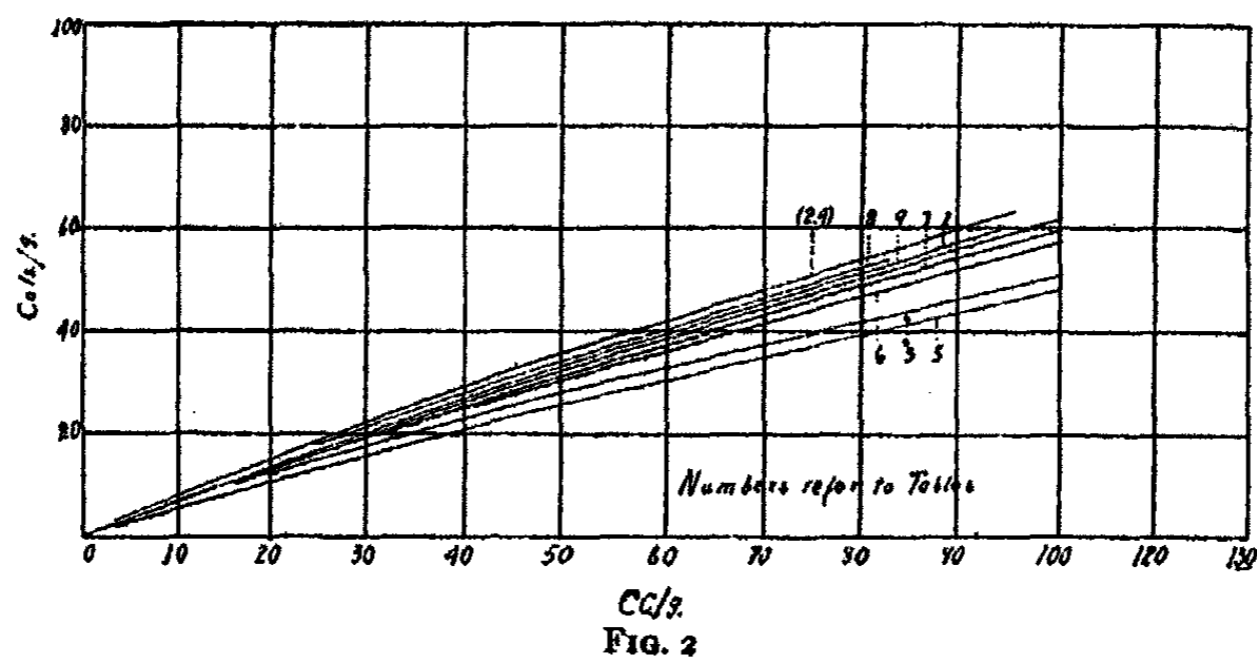


FIG. 2

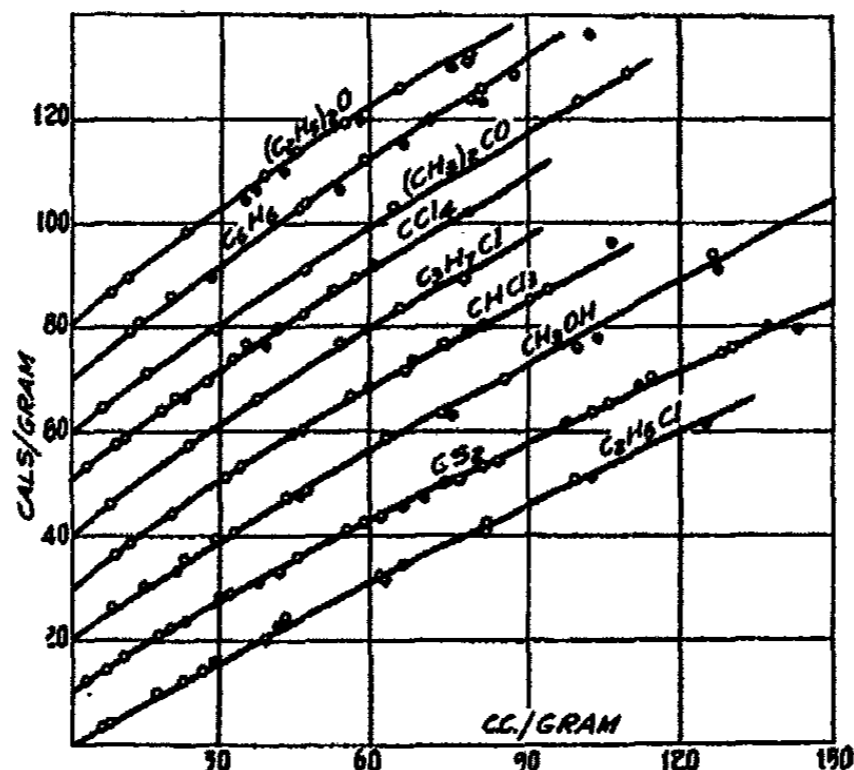


FIG. 3

next one to it, giving the system of curves in Fig. 3. The data obtained by Lamb and Coolidge at 0° are also indicated by the points, x . When the values of $\log n$ are plotted against the corresponding values of $\log x$, we get the curves in Fig. 4, from which the experimental values show slight, if any, deviations. From the position and slopes of these lines, (Fig. 5), we obtain the constants of the equation:

$$\log h = \log m - n \log X, \text{ or } h = m X^n.$$

The constants obtained in this way have been used to calculate the values of h which are given in the sixth column of each Table. In the seventh col-

umn are placed the differences, Δ , between the observed and calculated values. In case that more than one series of experiments was made with the same vapor, the same sample of charcoal was used. The fact that all of the points fall almost exactly upon the curve shows that the vapor is without influence upon the adsorption power of the charcoal.

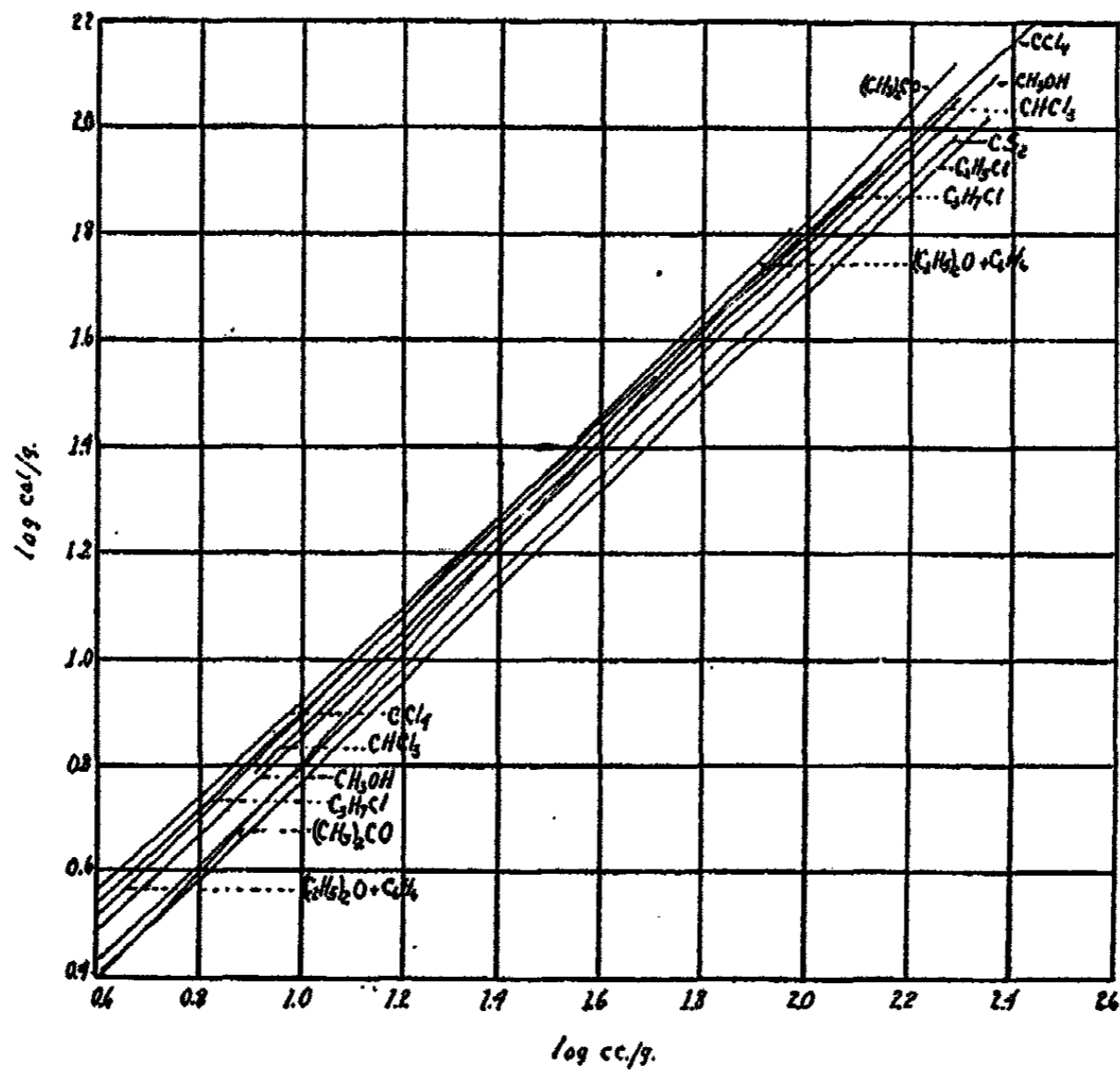


FIG. 4

Reproducibility and Reliability of Results

The results presented in Tables I to IX, and in Figs. 2 to 5, have been obtained with various weights of charcoal, some fresh, others previously used, and with variations in time and quantity of vapor admitted to the charcoal. The agreement between data on a fresh sample and on one which has been used is excellent. The agreement between duplicate runs for a given liquid is as good as that between the individual experiments. This is shown by Figs. 3 to 6. At most, the deviations are very slight. In general, the data of Lamb and Coolidge, indicated by points, x , are seen to be in close agreement.

These observations indicate that the total quantity of heat evolved during adsorption by gas-free charcoal is definite and reproducible. It is not affected by the manner in which the vapor is added, whether it is added slowly or rapidly, all at once, or in small portions. It is independent of the previous

history of the charcoal, provided the charcoal is previously evacuated at 550° . The calorimeter reading usually indicated adsorption equilibrium within eight to twenty minutes, and no appreciable "creeping" was ever observed. Vapors, such as carbon tetrachloride and chloroform, which are known to

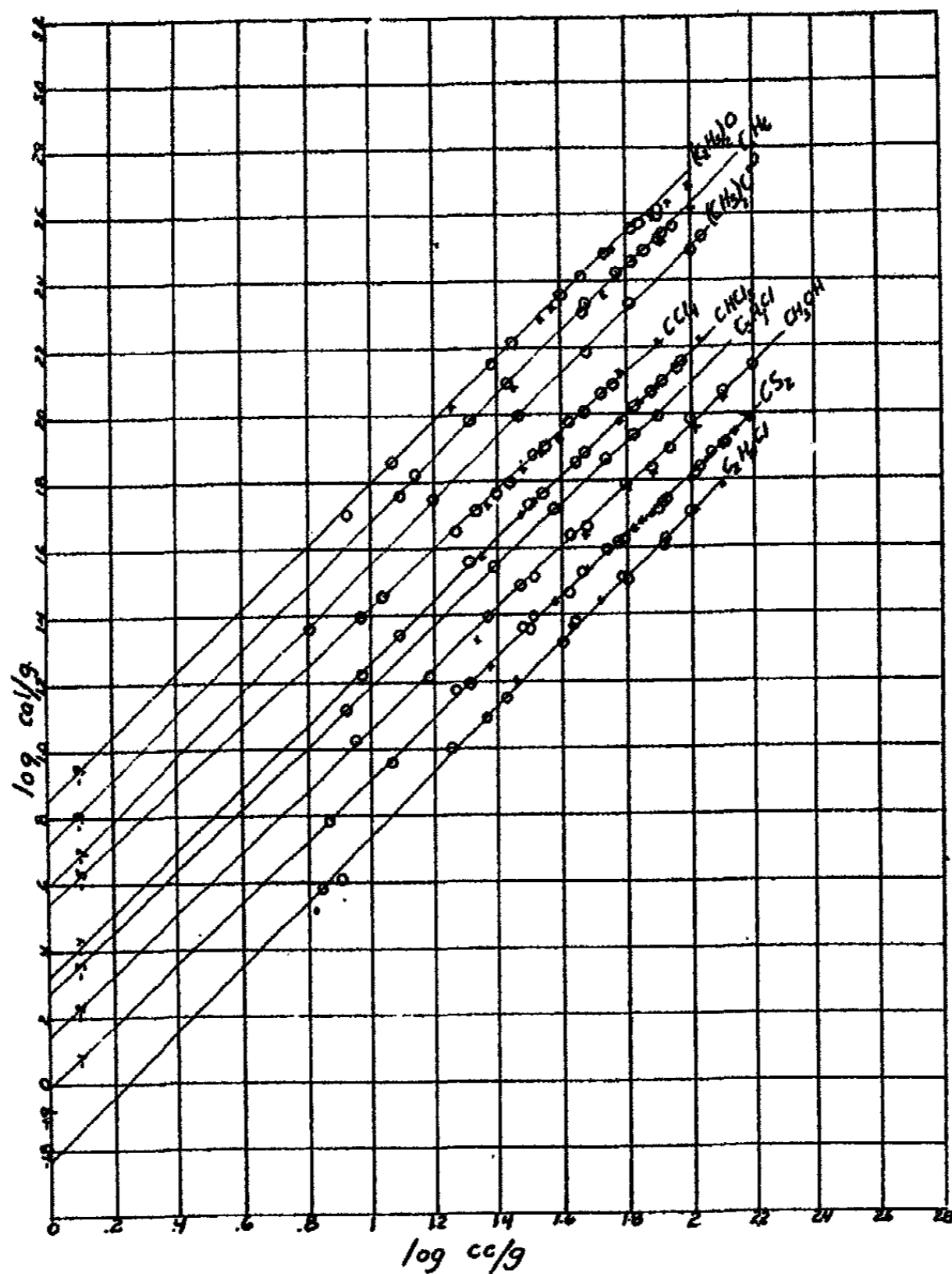


FIG. 5

poison charcoal, do not appear to reduce appreciably the quantity of heat evolved when a given volume of vapor is adsorbed in a subsequent run on the same sample. This is contrary to the observation of Lamb and Coolidge, who report that vapors studied with poisoned samples of charcoal give values for the heat evolved which are about 10 percent lower than with fresh samples.

Discussion of Results

In attempting to calculate the molecular heat of adsorption, h_m , from the data, we might simply solve for h in the equations,

$$h = mX^n,$$

after substituting for X , the volume of a gram molecule of the vapor, 22410 cc., and making use of the characteristic constants, m and n , obtained from the logarithmic plot. The resulting value for h , which would be the molecular heat of adsorption per one gram of charcoal, is impossible from a practical standpoint. In arriving at their values for h_m , Lamb and Coolidge chose to express it as the heat evolved when one mol of vapor is adsorbed by 500 g. of charcoal. This choice follows directly and conveniently from the fact that 1/500 mol of vapor is equivalent, in cc., to the average mid-point of the range of volume of vapor adsorbed by one gram of their charcoal. This mid-point they designate as 44.6 cc. In order the better to compare the results obtained by the two methods, we have made our calculations on the same basis as that used by Lamb and Coolidge. The results obtained by both methods are given in Table X. In making this comparison we must bear in mind that we have no knowledge of the mineral content of the charcoal which they have used.

TABLE X

Summary of Calorimetric Results on "Acid Washed," "Ash Free" Charcoal at 25°

| Vapor | Mol. Vol. | | n | m | | h_m | |
|-------------------------------------------------|-----------------|--------------|--------|-----------|--------------|-----------|------------------------|
| | Liq. 25° cc. | 25° Expt. | | 0° L-C | 25° Expt. | 0° L-C | 25° Expt. K-cal. |
| C ₂ H ₅ Cl | 71.1* | 0.9700 | 0.9150 | 0.5862 | 0.7385 | 11.5 | 12.0 |
| CS ₂ | 60.7 | 0.9110 | 0.9205 | 0.7861 | 0.7525 | 12.5 | 12.5 |
| CH ₃ OH | 40.7 | 0.9111 | 0.9380 | 0.8730 | 0.7420 | 13.9 | 13.1 |
| (CH ₃) ₂ CO | 73.9 | 0.9534 | — | 0.7713 | — | 14.4 | — |
| CHCl ₃ | 80.7 | 0.9350 | 0.9350 | 0.8295 | 0.8295 | 14.5 | 14.5 |
| C ₂ H ₇ Cl | 89.0 | 0.9115 | — | 0.9441 | — | 15.4 | — |
| CCl ₄ | 97.1 | 0.8780 | 0.9300 | 1.1070 | 0.8930 | 15.4 | 15.3 |
| C ₆ H ₆ | 89.4 | 0.9569 | 0.9590 | 0.828 | 0.774 | 15.7 | 14.7 |
| (C ₂ H ₅) ₂ O | 104.7 | 0.9353 | 0.9215 | 0.9044 | 0.9170 | 15.8 | 15.5 |

*Estimated.

Since the ground covered in this work is practically the same as that covered by Lamb and Coolidge, we can, in the discussion of these results, as well as of those that follow, do little more than make a comparison of the results obtained at the two temperatures by two entirely different methods. Perhaps the most striking relation to be observed in Table X is that for the calculated values of the molecular heats of adsorption, h_m . Except for ethyl chloride, methyl alcohol and benzene, the values are almost, if not identical. The molecular volume of ethyl chloride at 25° had to be estimated, and, hence, calculations depending upon it should have little weight. Omitting ethyl

chloride and carbon bisulphide, the values of h_m calculated for 25° do increase with increase in the molecular volume of the liquid. It will be observed also that the value of n is always less than unity. Even including the value of n for benzene, the maximum deviation from the mean value, 0.918, is only 5.6 percent. The values of m vary much more widely than do those of n , and, furthermore, there is a decided tendency for m to be small when n is large. Except for chloroform, the values of these constants seem to be dependent upon the temperature. In general, as the value of m increases with the temperature that of n decreases. The reverse relation is equally true. Lamb and Coolidge⁸ have shown by a graph that there is a decided relation between the values of $1-n$ and the boiling points of the liquids. They state that this parallelism indicates that the higher the boiling point of the liquid, the less marked is the "fatigue." No parallelism between n or m and any physical property of the liquids is directly apparent from our data.

No final conclusion as to the effect of temperature upon the molecular heat of adsorption can be drawn from the comparison of the data obtained at 0° and 25° . It suffices to say that the effect of temperature, in general, is not marked.

From a theoretical standpoint, the views regarding the effect of temperature upon the heat of adsorption are conflicting. In the first place, according to Lorentz and Lande,¹⁹ but in opposition to the views of Eucken,²⁰ the adsorption potential, which is really the heat of adsorption, should, in general, vary with the temperature. Secondly, it can be shown that the isosteres, obtained by plotting the values of the $\log p$ against the reciprocal of the absolute temperature, are in general for any one vapor linear and parallel, and, therefore, are of the same slope. If the value of $Rd \ln p/d(1/T)$ does not vary with the temperature, we should expect the heat of adsorption to be independent of the temperature and concentration. One objection to the use of the isosteres as a means of calculating the heat of adsorption is the fact that the values thus calculated are often too low and they do not include that appreciable part of the range of adsorption where p is too small to be measured accurately.

Lamb and Coolidge⁸ maintain that the process of adsorption may be considered as taking place in two steps: first, a compression of the vapor to such a point that liquefaction ensues, and second, a further compression of this liquid by the attractive forces of the adsorbent. The observed heat of adsorption will then be made up of two quantities, the heat of vaporization of the liquid, and that which may be designated as the *net* heat of adsorption. The latter quantity they showed to be proportional to the heat of compression of the liquid under high pressure. In accordance with this theory, the effect of temperature upon the heat of adsorption will be the result of two effects: one upon the heat of vaporization, and the other upon the heat of compression.

The molecular heats of adsorption of each of the nine vapors have been calculated for 25° . They are included with related data in Table XI. The

¹⁹ Lorentz and Lande: *Z. anorg. Chem.*, 125, 47 (1922).

²⁰ Eucken: *Ber.*, 12, 345 (1914).

second column contains the values for the molecular heats of adsorption when 1 cc. of liquid is adsorbed by 10 g. of charcoal; column 3 contains the molecular heats of vaporization, and column 4 the net heats of adsorption.

TABLE XI

Relation between Heats of Adsorption and Heats of Compression at 25°

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-------------------------------------------------|---------|---------|---------|-----------------------------|--------------------------|---------------------------------------|--------------------------|---------------------------------------|
| | h | Q | h-Q | h-Q | $\frac{dQ}{dP}$ | $\frac{\text{col. 5}}{\text{col. 6}}$ | $\frac{dQ}{dP}$ | $\frac{\text{col. 5}}{\text{col. 8}}$ |
| Vapor | K. cal. | K. cal. | K. cal. | ^{1 cc.} K. cal. | ^{1 cc.} cal. | ^x 1000 at. | ^{1 cc.} cal. | ^x 100 at. |
| C ₂ H ₅ Cl | 11.85 | 5.96* | 5.88 | 0.0828 | 0.01210 | 6.8 | 0.00351 | 23.6 |
| CS ₂ | 12.77 | 6.45 | 6.32 | 0.1041 | 0.00865 | 12.0 | 0.00343 | 30.8 |
| CH ₃ OH | 13.69 | 8.95 | 4.74 | 0.1165 | 0.00893 | 13.0 | 0.00351 | 35.0 |
| (CH ₃) ₂ CO | 14.74 | 7.66 | 7.08 | 0.0958 | 0.01050 | 9.1 | 0.00383 | 25.1 |
| CHCl ₃ | 14.97 | 7.72 | 7.25 | 0.0896 | 0.00914 | 9.8 | — | — |
| C ₂ H ₇ Cl | 15.90 | 6.90† | 9.00 | 0.1011 | 0.00837 | 12.1 | — | — |
| CCl ₄ | 16.90 | 7.72 | 9.18 | 0.0945 | 0.01260 | 7.5 | — | — |
| C ₆ H ₆ | 16.14 | 8.03 | 8.11 | 0.0907 | 0.00872 | 10.4 | — | — |
| (C ₂ H ₅) ₂ O | 16.62 | 6.44 | 10.18 | 0.0972 | 0.01186 | 8.2 | 0.00316 | 30.4 |
| Average | | | | 0.0969 | 0.0101 | 10.3 | 0.00350 | 29.0 |

*Mol. vol. estimated.

†Calculated from vapor pressure data.

TABLE XII

Relation between Heats of Adsorption and Heats of Compression at 0°

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-------------------------------------------------|---------|-------------------|---------|---------|------------------|---------------------------------------|------------------|---------------------------------------|
| | h. | Q. | h-Q | h-Q | $\frac{dQ}{dP}$ | $\frac{\text{col. 5}}{\text{col. 6}}$ | $\frac{dQ}{dP}$ | $\frac{\text{col. 5}}{\text{col. 8}}$ |
| Vapor | K. cal. | K. cal. | K. cal. | K. cal. | ^{1 cc.} | ^x 1000 at. | ^{1 cc.} | ^x 1000 at. |
| C ₂ H ₅ Cl | 12.33 | 6.22 ^a | 6.11 | 0.0864 | 0.0101 | 8.5 | 0.00314 | 27.5 |
| CS ₂ | 12.63 | 6.83 | 5.80 | 0.0991 | 0.0073 | 13.5 | 0.00326 | 30.2 |
| CH ₃ OH | 12.95 | 9.33 | 3.62 | 0.0908 | 0.0076 | 12.0 | 0.00312 | 28.9 |
| C ₂ H ₅ Br | 14.33 | 6.85 ^b | 7.48 | 0.1020 | 0.0086 | 11.9 | 0.00349 | 29.2 |
| C ₂ H ₅ I | 14.25 | 7.81 ^b | 6.44 | 0.0815 | 0.0074 | 11.0 | 0.00312 | 26.1 |
| CHCl ₃ | 14.93 | 8.00 | 6.93 | 0.0875 | 0.0071 | 12.3 | — | — |
| HCOOC ₂ H ₅ | 15.42 | 8.38 | 7.04 | 0.0901 | 0.0087 | 10.3 | — | — |
| C ₆ H ₆ | 15.17 | 7.81 | 7.36 | 0.0850 | 0.0074 | 11.5 | — | — |
| C ₂ H ₅ OH | 14.98 | 10.65 | 4.33 | 0.0768 | 0.0066 | 11.6 | 0.00269 | 28.2 |
| CCl ₄ | 16.09 | 8.00 | 8.09 | 0.0856 | 0.0076 | 11.3 | — | — |
| (C ₂ H ₅) ₂ O | 16.09 | 6.90 | 9.19 | 0.0803 | 0.0097 | 8.3 | 0.00298 | 26.9 |
| Average | | | | 0.0877 | 0.00801 | 11.1 | 0.00311 | 28.1 |
| Mean deviation | | | | +7.4% | | ±10% | | ±4% |

In general, the net heats of adsorption are, for the most part, of the same magnitude as the heats of vaporization. They vary from half as much for methyl alcohol to a half more for ether and propyl chloride. While the heats of vaporization of all liquids are less at 0° than at 25°, the net heats of adsorption are greater at 25° than at 0°. The one exception to this rule is ethyl chloride. This exception may be apparent, rather than real, since the calculation of h involved the calculation of the molecular volume of ethyl chloride as a liquid at 25°. The value of Q , the heat of vaporization, of ethyl chloride, may also be in error, since its value was obtained from existing vapor pressure data. Lamb and Coolidge report the heat of vaporization of benzene at 0° to be 7.81 K. cal. This value is much smaller than the values²¹, 8.28 and 8.51, as given by Regnault and Young, respectively. The data obtained by these two investigators is given in Table XII for comparison.

The net heats of adsorption per 1 cc. of liquid on 10 g. of charcoal at 25°, (Col. 5), were obtained by dividing the net molecular heat of adsorption by the molecular volume of the liquid at 25°. It is evident that these net heats of adsorption per 1 cc. of liquid are all very nearly the same, the average deviation from the mean, 0.0969 K. cal., being only 7.1 percent. Except for ethyl chloride, these net heats per cc. are all higher than the corresponding values at 0° by about 10 percent. The mean deviation is practically the same at both temperatures. Such a small deviation led Lamb and Coolidge to believe that the net heats of adsorption must be due to the attractive forces of the charcoal, and that for a given amount of capillary space the heat liberated is identical, or nearly so, for all liquids.

Following the methods of our predecessors, we have calculated the heat of compression, in small calories, per atmosphere per cc. of liquid at atmospheric pressure. This calculation was made by the use of the relation:

$$\frac{dQ}{dT} = \left(\frac{dv}{dP} \right) : \frac{T}{42.7}$$

The values of $\frac{dv}{dT}$ were obtained by substituting the values of the temperature and the constants in the expression obtained by differentiating series formulae of the type: $v_t = v_0(1 + \alpha t + \beta t^2 + \gamma t^3)$, as given in the Landolt-Börnstein Tables. In every case the values are somewhat higher than the corresponding values at 0°. This seems highly significant, since it may afford an explanation why the heat of adsorption might not change with temperature. That is, the change in the heat of vaporization may be compensated by a corresponding change of opposite sign in the heat of compression.

The quotients of the net heats of adsorption divided by the heats of compression give us the attractive forces of the charcoal acting on the various liquids. These quotients are given in column 7 of Table XI. The average value of the attractive forces is about 10000 atmospheres. The comparison of these values with those obtained for 0° show clearly that these forces are diminished with rise in temperature, and in some cases markedly so. Because

²¹ Landolt and Börnstein: "Tabellen."

of this high pressure, Lamb and Coolidge state that we are not justified in using heats of compression at 1 atmosphere in making these computations; that instead we should use the mean heats of compression obtained by integration over the whole pressure range covered. They have calculated the attractive forces of some of their vapors at 0° from the heats of compression computed by Bridgman²³ at pressures up to 12000 atmospheres. Five of our vapors were studied by Bridgman at 20°, 40°, 60° and 80°. The values of the heats of compression at 25° have been interpolated and are given in column 8. The average value is about 12 percent higher than at 0°; the individual values show an even greater constancy.

If we now divide the net heats of adsorption by these better values of the heats of compression, we obtain the attractive forces given in column 9. The average value of the attractive force of carbon for these five vapors is 29000 atmospheres, or about 3.1 percent higher than for the average of the seven studied at 0°. The rather considerable increase in the attractive force of carbon for methyl alcohol and ether is significant.

Whether or not the attractive force exerted by charcoal on all liquids is the same and independent of the temperature is still a question. We know relatively little regarding the conditions prevailing in liquids under high pressures. Furthermore, we know still less of the conditions existing when these liquids are under high pressures and at the same time in contact with the attractive forces of a powerful adsorbent. For example, Bridgman states that pure acetone solidifies at 20° when under a pressure of 8000 atmospheres. At what temperature would it solidify under this same pressure when in contact with porous charcoal? This we cannot answer.

Summary

1. A new calorimetric method has been devised by which it is possible to measure heats of adsorption at any temperature. It permits the use of temperatures at which the liquid phase is absent, and thus prevents the introduction of the thermal effect due to ordinary condensation.
2. The method possesses three important features. (a) Objectionable condensation effects are eliminated by having the calorimeter at the same temperature as that of the vapor to be adsorbed. (b) The charcoal bulb is of such a design that the heat evolved is quickly conducted outward to the calorimeter liquid. (c) The rise in temperature of a known weight of oil is read by a sensitive thermoelement.
3. The heats of adsorption of nine vapors on charcoal have been measured at 25°. The heat effects were found to be easily reproducible, and they are independent of the rate of adsorption of the vapor and of the previous history of the charcoal.
4. The heats of adsorption of these vapors are in close agreement with those obtained by Lamb and Coolidge for the same vapors at 0°.

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The State University of Iowa.*

²³ Bridgman: Proc. Am. Acad., 49, 1 (1913).

35-145

THE ROLE OF PHOSPHATES ON THE TAKING UP OF DYES BY MORDANTS

BY CHARLES E. WHITE AND NEIL E. GORDON

Many attempts have been made to advance a satisfactory theory to explain the effect of salts upon the dyeing process, but none of these have proved entirely satisfactory. One reason for this seems to be the lack of quantitative data based on investigations in which sufficient attention has been given to a control of the variables. The object of this investigation was to obtain quantitative data under such carefully controlled conditions that it might be possible to determine definitely the effect of phosphates on the taking up of dyes by mordants.

Materials used

The hydrous oxide gels of iron, aluminum and chromium were used throughout the experiment. These were prepared by dissolving seventy-five grams of the respective chlorides in five liters of water at a temperature of fifty degrees centigrade and then very dilute ammonium hydroxide was added until all of the metal had precipitated. The gel was washed free from chlorides by decantation. This usually required six or seven days. In most of the experiments the gel was used mixed with such a quantity of water that it could be readily drained free from a fifty cubic centimeter pipette from which the tip had been cut off in order to allow passage of the large particles of gelatinous material. Where it was objectionable to have such a large quantity of water present the gel was filtered by suction until all the water possible had been removed. The gel in the resulting condition was weighed up on the balance in a stoppered weighing bottle. The silica gel was furnished by the Davison Chemical Company. Before using, it was ground small enough to pass a one hundred mesh sieve, washed by decantation and allowed to dry at room temperature.

The water content of the gel was determined by heating a sample for twenty-four hours at 105° C. The iron, aluminum and chromium gels that were in a condition to be measured in a pipette contained about 98 per cent water.

The dyes were donated by E. I. du Pont de Nemours and Company. The acid dye, Orange II, is a sodium salt and the basic dye Crystal Violet is a chloride, potassium di-hydrogen phosphate, the salt, was J. T. Baker's C. P. material.

Experimental Procedure

In the adsorption of dyes by gels Gordon and Marker¹ have shown that equilibrium is reached if the dye and the gel are heated to 100° C for two hours with frequent shaking. Gordon and Starkey² have shown that in order to

¹ Ind. Eng. Chem., 16, 1186 (1925).

² Soil Science, 14, p. 449 (1922).

obtain maximum adsorption of potassium di-hydrogen phosphate by inorganic gels the mixture must be shaken almost continuously for seventy-two hours. Thus when it was desired to have comparable results with both the dye and phosphate, the solutions were put into 250 cc. ground-glass stoppered bottles, heated at 100° for two hours, then shaken continuously for three days in a mechanical shaker.

After this the solution was analyzed for materials unadsorbed. The solution was separated from the gel by an ultra filter. This was made by pouring the mixture of gel and solution over a filter paper until the paper had become thickly coated with gel. The whole solution was then filtered through this.

Determination of Adsorbed Materials

The adsorption was determined by analyzing the solution before mixing with the gel and then again after adsorption had taken place. The difference between these determinations was called the amount of material absorbed. The dye was determined by titration with titanium tri-chloride according to the general directions in Knecht and Hibbert's "Manual of Volumetric Dye Analysis." Specific directions were furnished by E. I. du Pont de Nemours and Company. Their directions are as follows:

"DuPont Orange II: Dissolve .2 gms. dye in 100 c.c. water and 35 c.c. of sodium tartrate (25%). Boil gently three minutes and titrate hot under CO₂ with .05N TiCl₃ solution. The final color change is from red to gray or brown and is sharp. The titration should be carried out slowly as the end point is approached."

In determining potassium, and the phosphate radical in Orange II solutions, it was necessary first to remove the dye by precipitation with HCl or to decompose it by boiling with aqua-regia. Both methods were used and the latter found to be the most satisfactory. The potassium was determined by precipitation with platonic chloride according to the Lindo-Gladden method. The phosphate was determined by the ammonium molybdate method. In the case of Crystal Violet the dye was removed by precipitation with sodium hydroxide.

The hydrogen ion concentration of all clear solutions was determined by means of the Bailey Electrode. A normal calomel electrode was used with this and the readings taken on a Leeds and Northrup "Student Type" potentiometer.

In order to obtain the pH of the dye solutions and of solutions containing any colloidal material a modified form of the Hildebrand type electrode was used. The electrode was a single platinum wire coated with platinum black. Before using this it was saturated with hydrogen by electrolysis in a sodium hydroxide solution. It was found that this treatment insured much steadier readings in dye solutions. In making a determination the solution was saturated with hydrogen before the electrode was immersed in it. For Crystal Violet solutions and clear solutions the readings of this electrode could be checked with those of the Bailey electrode. But with Orange II solutions this is not true. With Orange II all readings were determined in duplicate on the

electrode described above as soon as a steady reading could be obtained after the electrode was immersed in the solution. While it is not claimed that these values are absolute, they are the best it is possible to obtain under these conditions and they allow excellent comparison for this work.

The Adsorption of Crystal Violet by Silica, Iron and Aluminum Gels in the Presence of Phosphates

Tables I-VI show a comparison of the Crystal Violet dye adsorbed with KH_2PO_4 present and when no salt was used. In these experiments the pH was varied by using sulphuric acid and sodium hydroxide. The solutions used were .05 per cent dye and 0.5 N KH_2PO_4 .

TABLE I

The Effect of Phosphates on the Adsorption of Crystal Violet (a basic dye) by Silica Gel

| pH of salt solution | pH of bath after ads. | Mgm. of dye ads. per gm. dry gel | |
|---------------------|-----------------------|---------------------------------------|---------------|
| | | with KH_2PO_4 present | no salt pres. |
| 1.1 | 1.05 | 1.1 | 1.1 |
| 1.42 | 1.52 | 2.3 | 2.4 |
| 2.74 | 2.75 | 2.5 | 3.1 |
| 4.62 | 3.14 | 3.2 | 4.1 |
| 4.67 | 3.16 | 3.5 | 4.2 |
| 6.68 | 4.43 | 7.3 | 4.6 |
| 6.98 | 4.70 | 9.0 | 4.7 |

TABLE II

The Effect of Phosphates on the Adsorption of Crystal Violet (a basic dye) by Aluminum Gel

| pH of salt solution | pH of bath after ads. | Mgm. dye ads. per gm. dry gel | |
|---------------------|-----------------------|----------------------------------|--------------|
| | | KH_2PO_4 present | without salt |
| 1.52 | 2.91 | — | 3.0 |
| 2.81 | 5.36 | 49.2 | 4.0 |
| 4.63 | 5.98 | 173.4 | 7.0 |
| 6.12 | 6.12 | 216.5 | 13.0 |
| 6.49 | 6.30 | 439.3 | 16.0 |
| 6.85 | 6.54 | 449.1 | 18.0 |

TABLE III

The Effect of Phosphates on the Adsorption of Crystal Violet (a basic dye) by Iron Gel

| pH of salt solution | pH of bath after ads. | Mgm. dye ads. per gm. dry gel | |
|---------------------|-----------------------|--------------------------------|--------------|
| | | KH_2PO present | without salt |
| 2.59 | 5.27 | 378 | 28.0 |
| 4.45 | 6.04 | 460.9 | 40.0 |
| 6.12 | 6.14 | 886.8 | 46.2 |
| 6.49 | 6.42 | 1041.4 | 47.5 |
| 6.85 | 6.81 | 1118.3 | 48.0 |

It is seen from the above data that the effect of the phosphate salt added is to increase the adsorption of the basic dye. The pH could not be carried any higher due to the dye precipitating out of solution. Iron gel seems to be the best adsorbent for the basic dye and as will be noted in the following tables it is also the best adsorbent for phosphates. Both the potassium and the phosphate adsorbed in the above experiment were determined. The data are for all three gels.

TABLE IV

The Effect of Crystal Violet Dye on the Adsorption of Potassium Acid Phosphate by Silica Gel

| pH of bath after ads. | Mgm. adsorbed per gram of dry gel. | | | |
|--------------------------|-------------------------------------|--------------------------------|-----------------------|------------------|
| | PO ₄ ads. dye present | PO ₄ ads. no dye | K ads. dye present | K ads. no dye |
| 1.05 | -0.8 | 2.7 | -0.2 | -2.7 |
| 1.52 | -0.6 | 0.5 | -0.2 | -2.4 |
| 2.75 | -0.5 | -0.3 | -0.16 | -1.6 |
| 3.14 | -0.1 | -0.1 | -0.13 | -1.4 |
| 3.16 | 0.1 | -2.0 | 0.01 | -1.5 |
| 4.43 | 0.2 | -2.3 | 0.5 | -0.2 |

TABLE V

The Effect of Crystal Violet Dye on the Adsorption of Potassium Acid Phosphate by Aluminum Gel

| pH of bath after ads. | Mgm. adsorbed per gram of dry gel. | | | |
|--------------------------|-------------------------------------|--------------------------------|-----------------------|------------------|
| | PO ₄ ads. dye present | PO ₄ ads. no dye | K ads. dye present | K ads. no dye |
| 2.91 | 127.8 | 318.5 | 4.4 | 4.7 |
| 5.36 | 124.9 | 249.0 | 7.1 | 9.4 |
| 5.98 | 110.9 | 233.0 | 11.4 | 10.6 |
| 6.12 | 101.2 | 227.5 | 9.4 | 10.8 |
| 6.30 | 104.3 | 223.3 | 9.5 | 11.1 |
| 6.54 | 98.8 | 218.0 | 9.9 | 11.5 |

TABLE VI

The Effect of Crystal Violet Dye on the Adsorption of Potassium Acid Phosphate by Iron Gel

| pH of bath after ads. | Mgm. adsorbed per gram of dry gel | | | |
|--------------------------|-------------------------------------|--------------------------------|-----------------------|------------------|
| | PO ₄ ads. dye present | PO ₄ ads. no dye | K ads. dye present | K ads. no dye |
| 5.27 | 272.5 | — | 17.9 | — |
| 6.04 | 254.2 | — | 26.1 | 91.0 |
| 6.14 | 258.6 | — | 28.7 | 90.0 |
| 6.42 | 247.3 | 339.0 | 30.2 | 82.0 |
| 6.81 | 255.6 | 276.0 | 28.1 | 76.0 |

In every case it is shown that even though the dye is very much more highly adsorbed with the phosphate present, the PO_4 adsorption is not great enough to account for the high adsorption of the dye. It is believed that the salt increases the size of the dye particle to colloidal dimensions and then it is merely filtered out of solution by the gelatinous particles of metallic oxides.

It will be noted in subsequent data that the action of phosphates with acid dyes is directly opposite to that with basic dyes.

Adsorption of Orange II (an acid dye) by Silica, Iron, Aluminum and Chromium Gels

With silica gel there was no adsorption of the acid dye Orange II either with or without a salt present.

Table VII shows that with aluminum gel the adsorption of Orange II was greatly decreased by the presence of the phosphate. In this experiment the pH was varied with sulphuric acid and sodium hydroxide. The solution used was 0.5 per cent dye and 0.05 N KH_2PO_4 .

TABLE VII
The Effect of Potassium Acid Phosphate on the Adsorption of Orange II by Aluminum Gel

| pH of original salt solution | Final pH of bath | Mgm. dye ads. per gm. dry gel. | |
|------------------------------|------------------|--------------------------------|-----------------|
| | | Phosphate present | no salt present |
| 2.68 | 5.05 | 38 | 279 |
| 3.18 | 5.51 | 26 | 186 |
| 3.38 | 5.43 | 27 | 185 |
| 4.48 | 5.73 | 15 | 177 |
| 6.49 | 6.02 | 14 | 170 |
| 7.02 | 6.56 | 1 | 166 |

This data are illustrated more vividly in Fig. 1.

It is remarkable that the small amount of salt added to the dye bath should make such a marked decrease in the adsorptive power of the gel. It might be expected that the gel has preferentially adsorbed the phosphate, but the following data show that there is also a great decrease in the phosphate adsorption.

TABLE VIII
The Adsorption of Potassium Acid Phosphate by Aluminum Gel in the Presence of Orange II Dye

| pH of bath after ads. | Mgm. adsorbed per gm. of dry gel | | | |
|-----------------------|----------------------------------|---------------------------|--------------------|---------------|
| | PO_4 ads. dye present | PO_4 ads. no dye | K ads. dye present | K ads. no dye |
| 5.05 | 143.0 | 258.5 | 00 | 9.0 |
| 5.51 | 117.6 | 244.0 | 00 | 9.8 |
| 5.43 | 105.8 | 247.5 | 00 | 9.7 |
| 5.73 | 96.7 | 238.0 | 4.67 | 10.2 |
| 6.02 | 75.7 | 231.5 | 6.12 | 10.6 |
| 6.56 | 46.3 | 217.5 | — | — |

A comparison of the phosphate adsorptions is given in Fig. 2.

The great decrease in the adsorption of the phosphate cannot be balanced by the very slight adsorption of the dye. The same phenomenal decrease in adsorption is noted in the following data on iron gel.

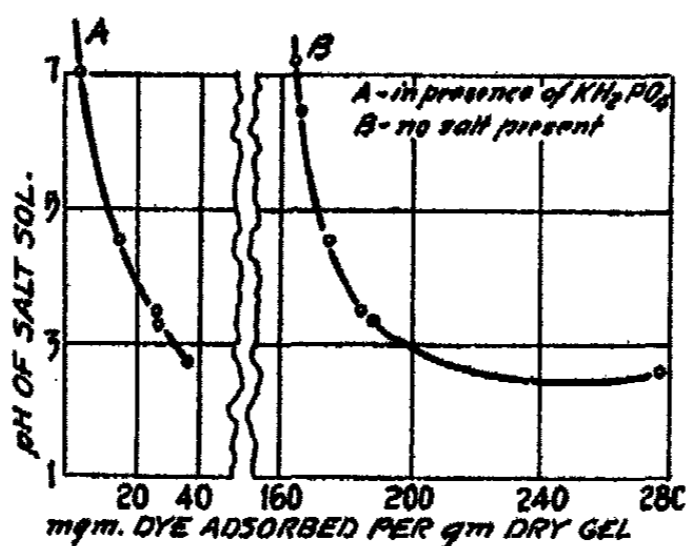


FIG. 1
Adsorption of Orange II by Aluminum Gel

TABLE IX

The Effect of Potassium Acid Phosphate on the Adsorption of Orange II by Iron Gel

| pH of original salt solution | pH of bath after ads. | Mgm. dye ads. per gm. dry gel | |
|------------------------------|-----------------------|-------------------------------|-----------------|
| | | phosphate present | No salt present |
| 2.75 | 6.09 | ∞ | 225 |
| 3.16 | 6.25 | ∞ | 80 |
| 4.66 | 6.42 | ∞ | 70 |
| 6.54 | 6.60 | ∞ | 63 |
| 7.05 | 6.79 | ∞ | 62 |

The phosphate and potassium adsorption was also decreased below normal even though no dye was adsorbed.

TABLE X

The Adsorption of Potassium Acid Phosphate by Iron Gel in the Presence of Orange II Dye

| pH of bath after ads. | Mgm. ads. per gram of dry gel. | | | |
|-----------------------|--------------------------------|--------------------|--------------------|---------------|
| | PO_4 ads. dye present | PO_4 ads. no dye | K ads. dye present | K ads. no dye |
| 6.09 | 211.1 | — | 21.4 | 91.0 |
| 6.25 | 200.5 | — | 24.3 | 88.0 |
| 6.42 | 188.6 | 340 | 25.1 | 83.0 |
| 6.60 | 160.3 | 330 | 23.6 | 80.0 |
| 6.79 | 130.6 | 319 | 19.1 | 74.0 |

In order to determine whether this decrease in adsorption was due to the PO_4 ion alone or to other ions present, an experiment was run where phosphoric acid was added to the dye solution. Varying amounts of the acid were used in order to vary the pH. Of course there might be expected a change in adsorption due to the varying concentration of the negative radical. In the following experiment one gram of Orange II dye was dissolved in 200 cc. of phosphoric acid solutions and added to 1.02 grams of gel.

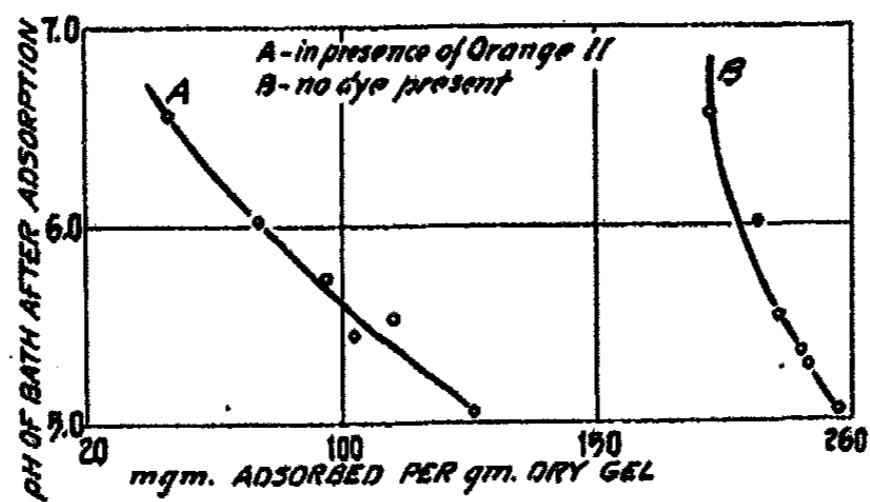


FIG. 2
Adsorption of Phosphate by Aluminum Gel

TABLE XI

The Effect of Phosphoric Acid on the Adsorption of Orange II by Iron Gel

| Final pH of bath | Mgm. per gram of dry gel. | | |
|---------------------|-------------------------------------|--------------------|----------|
| | PO_4 originally present | PO_4 ads. | Dye ads. |
| 4.30 | 263.5 | 233.5 | ∞ |
| 4.85 | 217.8 | 202.9 | ∞ |
| 5.16 | 164.0 | 153.9 | ∞ |
| 5.29 | 102.9 | 97.9 | ∞ |
| 5.36 | 92.3 | 86.6 | ∞ |
| 5.44 | 61.9 | 58.7 | ∞ |

Table XI shows conclusively that the elimination of the adsorption of the dye is due to the phosphate and not to the presence of other ions.

Having established the fact that the phosphate was the effective agent in decreasing the adsorption of the dye it became our problem to determine if possible just why the phosphate should do this.

Gordon and Marker¹ have shown that the taking up of Orange II by aluminum and iron gels is a chemical reaction and not merely a case of surface adsorption. According to this then the observed facts should offer explanation either on the basis that the phosphate is acting on the gel and preventing its reaction with the dye, or it is acting upon the dye in solution in such a manner that it prevents the reaction taking place.

¹ Ind. Eng. Chem., 16, 1186 (1925).

Taking the latter idea first, it was thought possible that the phosphate might have an effect of increasing the solubility of the dye in solution and thus making its taking up by the gel more difficult. So an experiment was run to determine this. It was found that at the concentrations of phosphates used in the experiment there was no detectable influence upon the solubility. But if a large quantity of phosphate is added, the solubility of the dye decreases and the dye may be precipitated out of solution. This would have the effect of increasing the adsorption by gels rather than decreasing it. Another thought was, that owing to a change in the thermodynamic environment of the solution on the addition of phosphate, it might take a longer time for the dye and gel to reach equilibrium. So an experiment was run in which the dye was allowed to remain in contact with the gel for a period of six months. Samples were removed at intervals for analysis.

Solutions of 0.5 per cent Orange II dye and .05 normal potassium dihydrogen phosphate were mixed with 1.08 grams of gel. This mixture was heated to boiling for four hours and placed in a mechanical shaker and agitated. This treatment was repeated at frequent intervals over a period of six months. The pH was varied with phosphoric acid and potassium hydroxide.

TABLE XII

The Result of allowing Orange II and Phosphate Solution to act on Iron Gel for a period of six months

| pH of dye bath Jan. 1 | pH of dye bath July 3 | Mgm ads. per gm. dry gel. | | | |
|-----------------------|-----------------------|---------------------------|-----------------|-----------------------------|-----------------------------|
| | | Dye ads. Jan. 1 | Dye ads. July 3 | PO ₄ ads. Jan. 1 | PO ₄ ads. July 3 |
| 5.02 | 5.46 | 00 | 00 | 232.3 | 219.6 |
| 5.27 | 5.69 | 00 | 00 | 229.4 | 238.7 |
| 5.66 | 5.87 | 00 | 00 | 202.7 | 206.8 |
| 5.86 | 5.95 | 00 | 00 | 191.0 | 207.3 |
| 5.95 | 6.07 | 00 | 00 | 187.1 | 171.7 |
| 5.71 | 6.07 | 00 | 00 | 146.3 | 164.0 |

The data show that there was no adsorption of dye under these conditions even after being in the presence of the gel for a period of six months. The phosphate adsorption changed only very slightly and the pH shows a correspondingly slight change. It was concluded then that the reason for phosphate cutting out the adsorption was not to be found in its effect upon the dye in the solution.

On the basis of the other idea mentioned above that the phosphate decreased the adsorption of acid dyes because of its effect upon the gel, it was thought possible that the phosphate might be adsorbed on the surface of the gel and thus prevent the gel reacting with the dye.

In order to determine this it was decided to run an experiment in which the gel would be allowed to adsorb the phosphate from the solution before adding the dye. If no adsorption took place it was thought it might be concluded that the phosphate coated the gel in such a way as to prevent its reacting with the dye.

.5 gram of gel and 100 cc. of potassium dihydrogen phosphate was boiled for two hours, then shaken for three days in a mechanical shaker. 25 cc. of the solution was then removed and tested for phosphates. Then 100 cc. of a one per cent dye solution were added and the mixture again boiled and shaken the same as before. The following results were obtained:

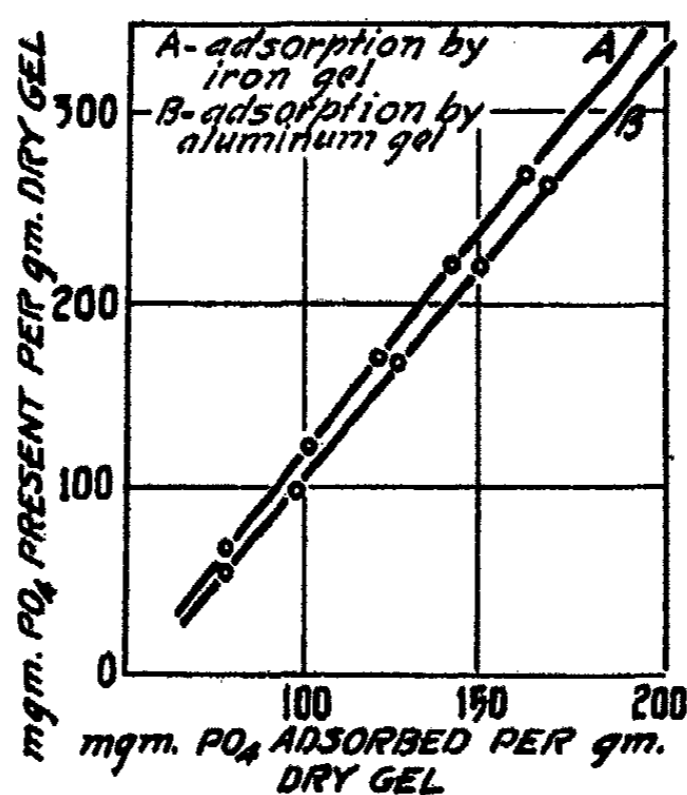


FIG. 3

The Relation between the Amount of PO_4 adsorbed and the Amount present in a Bath of Orange II Dye.

TABLE XIII

The Effect of Iron Gel adsorbing all the Phosphate from the Solution first, then adding Orange II

| Final pH of bath | Orig. PO_4 mgm per gm dry gel | PO_4 in supernatant liquid before dye added | Dye ads | Mgm PO_4 ads. per gm. dry gel in final bath |
|------------------|---------------------------------|-----------------------------------------------|---------|-----------------------------------------------|
| 5.53 | 63.7 | none | ∞ | 59.4 |
| 5.73 | 127.4 | trace | ∞ | 105.4 |
| 5.75 | 190.1 | quantity | ∞ | 126.8 |
| 5.86 | 254.8 | quantity | ∞ | 154.7 |
| 5.27 | 63.9 | none | ∞ | 59.7 |

It will be noted that there was no dye adsorbed even when there was no phosphate in the supernatant liquid when the dye was added. The data show, though, that some of the adsorbed phosphate was released to the solution after the dye was added. This might have been expected, since in Table XI it was shown that in the presence of Orange II the amount of phosphate adsorbed is proportional to the concentration of the solution. Hence when the solution was diluted with the dye we would expect some of the phosphate to be released. This point is illustrated in Fig. 3.

Since some phosphate was released to the solution this experiment does not prove conclusively its original purpose. It does show, however, that the dye will not replace the adsorbed phosphate on the gel. It then became important to know whether, if the dye was adsorbed first, the phosphate would displace it. In order to determine this the following experiment was performed.

150 cc. of a 0.75 per cent solution of Orange II was boiled with the gel for two hours and samples were removed for analysis. 100 cc. of 0.05 N KH_2PO_4 were then added to each solution. This was shaken for three days to attain equilibrium. The pH of the original dye solutions was varied by adding sulphuric acid and sodium hydroxide. The results of this experiment are given in Tables XIV and XV.

TABLE XIV

The Effect of allowing Aluminum Gel to adsorb Orange II first then adding Potassium Acid Phosphate to the Solution

| pH after dye ads. | pH of final bath | Mgm. adsorbed per gm. dry gel | | | |
|-------------------|------------------|-------------------------------|---------------------------|--------------|--------------------|
| | | dye ads. before salt added | dye ads. after salt added | dye released | PO_4 ads. |
| 5.2 | 4.8 | 439.4 | 119.5 | 373.9 | 150.7 |
| 5.3 | 4.9 | 311.1 | 24.3 | 286.8 | 119.1 |
| 5.56 | 5.2 | 67.0 | 15.0 | 52.0 | 86.9 |

TABLE XV

The Effect of allowing Iron Gel to adsorb Orange II first then adding Potassium Acid Phosphate to the Solution

| pH after dye ads. | pH of final bath | Mgm adsorbed per gm. dry gel. | | | |
|-------------------|------------------|-------------------------------|---------------------------|--------------|--------------------|
| | | dye ads. before salt added | dye ads. after salt added | dye released | PO_4 ads. |
| 5.05 | 4.56 | 407.6 | 24.4 | 383.2 | 166.0 |
| 5.11 | 5.42 | 245.7 | 21.6 | 224.7 | 141.0 |
| 5.48 | 5.69 | 9.7 | 2.0 | 7.7 | 114.4 |
| 5.49 | 5.65 | 9.7 | 2.0 | 7.7 | 120.0 |

The data show that a very high percentage of the dye is displaced by the phosphate. At first thought it would seem that if this were chemical replacement one equivalent of dye should be replaced by one equivalent of phosphate. These values were calculated and not found to agree in any case. This is as it should be for undoubtedly some of the dye was released on dilution of the solution. Or in other words some of the dye compound already formed is dissolved on the addition of the phosphate solution.

The data presented thus far seem to show that the effectiveness of the phosphate in reducing the adsorption of the dye is due to its effect upon the gel. The thought was then advanced that the phosphate covered the exterior

surface with an insoluble phosphate and did not leave any ferric hydroxide exposed to react with the acid of the dye. It is well known that iron and aluminum gels are precipitated in very large particles, and just as the reaction of sulphuric acid on lead is stopped by lead sulfate, here the reaction may be prevented by the formation of iron phosphate on the surface of the gel. If this concept is true we should be able to increase the adsorption of a salt by taking these larger particles of gel and breaking them apart so as to expose new surfaces.

In order to prove this point samples of iron and aluminum gels were allowed to reach a maximum adsorption with potassium acid phosphate. The gel was then removed and ground thoroughly in a mortar for ten minutes; it was then returned to the solution and placed in the mechanical shaker again. Samples were removed, before and after grinding the gel, for analysis. The pH of the solutions was varied by adding potassium hydroxide. 1.05 grams of gel (90 percent Fe_2O_3 and 74.5 percent Al_2O_3 respectively) were used with 200 cc. of 0.05 N KH_2PO_4 .

TABLE XVI
The Effect of Further Subdivision of the Particle of Aluminum Gel

| pH of original salt solutions | pH of bath before grinding | pH after grinding | Mgm. PO_4 ads. per gm dry gel | | |
|-------------------------------|----------------------------|-------------------|----------------------------------------|----------------|----------|
| | | | Before grinding | After grinding | Increase |
| 4.683 | 7.168 | 7.405 | 138.4 | 147.7 | 9.3 |
| 5.799 | 7.328 | 7.422 | 135.6 | 143.3 | 7.6 |
| 6.287 | 7.532 | 7.641 | 127.6 | 132.5 | 4.9 |
| 7.084 | 8.081 | 8.182 | 94.4 | 97.1 | 2.7 |
| 10.718 | 9.417 | 9.552 | 41.1 | 46.4 | 5.4 |

TABLE XVII
The Effect of Further Subdivision of the Particle of Iron Gel

| pH of original salt solutions | pH of bath before grinding | pH after grinding | Mgm. PO_4 ads. per gm dry gel | | |
|-------------------------------|----------------------------|-------------------|----------------------------------------|----------------|----------|
| | | | Before grinding | After grinding | Increase |
| 4.683 | 7.151 | 7.354 | 166.2 | 171.5 | 5.3 |
| 5.799 | 7.303 | 7.439 | 163.4 | 166.1 | 2.7 |
| 6.289 | 7.557 | 7.624 | 154.2 | 160.7 | 5.5 |
| 7.084 | 8.098 | 8.149 | 121.2 | 126.0 | 4.8 |
| 10.718 | 8.706 | 9.028 | 58.7 | 68.8 | 10.1 |

The difference in pH between the first and second column does not give the pH change corresponding to the phosphate adsorbed because quite a bit of water was added with the gel. In a total of 48.3 grams of gel plus water there was 47.3 grams of water. With the iron gel in the above experiment even after filtering there was considerable colloidal ferric phosphate in the solution. For the phosphate determination this was removed by saturating the solution with ammonium nitrate which precipitated the colloid. On filtering, the solution was perfectly clear.

The data given in the two preceding tables are presented in Fig. 4.

From these curves it is seen readily that there was quite a definite increase in the adsorption of phosphates by both iron and aluminum gels when new surfaces were exposed by crushing the gel particle. This seems to show that the surface of the gel, when maximum adsorption is reached, is coated with a definite film of phosphate which is impervious to more phosphate or dye under the existing conditions. But when one of these phosphate-coated particles is broken and a new surface exposed, more of the phosphate can be taken up

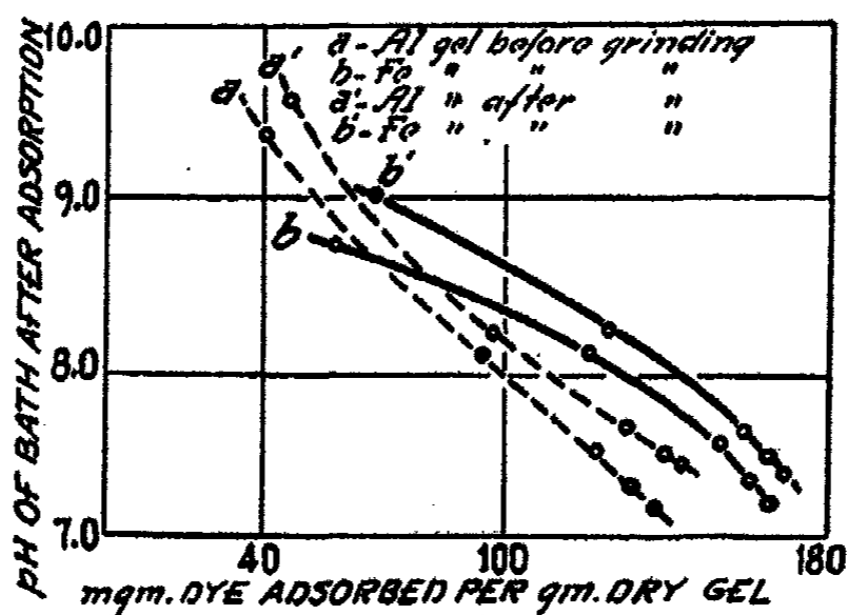


FIG. 4

The Effect of Further Subdivision of the Particles of Gel on Adsorption of Phosphates

from the solution. This might appear to be then the explanation of the fact that phosphates cut out the adsorption of an acid dye by iron gel. If the layer of phosphate formed cannot be penetrated by additional phosphate from phosphoric acid, then it is reasonable to suppose that the dye cannot penetrate the film. But in experiments following this where less phosphate was used and was still effective in preventing the adsorption of the dye, it is hardly conceivable that there is a sufficient amount of the phosphate radical present to cover the whole surface of the gel. These data, however, certainly seem to explain the always troubling assertion that there is apparently never a definite chemical equivalent relationship between the amount of material adsorbed and the amount of gel present. All of the preceding data were recalculated on the basis that the dry gel was 74.5 per cent Al_2O_3 and 90 per cent Fe_2O_3 respectively and no definite chemical combining ratios were found between the dye or salt adsorbed and the iron or aluminum present as gels. None should be expected according to the data presented in Tables XV and XVI because at all times there might be quite a large score of aluminum hydroxide or iron hydroxide within the gel particle that never comes in contact with the solution and hence cannot be acted upon.

In all of the data presented, the adsorption of the dye in phosphoric acid has been compared to the adsorption in sulphuric acid. In order to have a comparison of the effects of the ions Cl^- , SO_4^{--} and PO_4^{---} upon the ad-

sorption of Orange II, an experiment was run using hydrochloric, sulphuric and phosphoric acids of the same pH values to dissolve the dye, and iron, aluminum and chromium gels as adsorbing mediums. The same amounts of gel and the same percentage dye solution (0.5 per cent) were used in each case. The results are given in grams of dye adsorbed per gram of dry gel. The gel in this state in the case of iron is 90 per cent Fe_2O_3 , that of aluminum 74.5 per cent Al_2O_3 and chromium 70.4 per cent Cr_2O_3 .

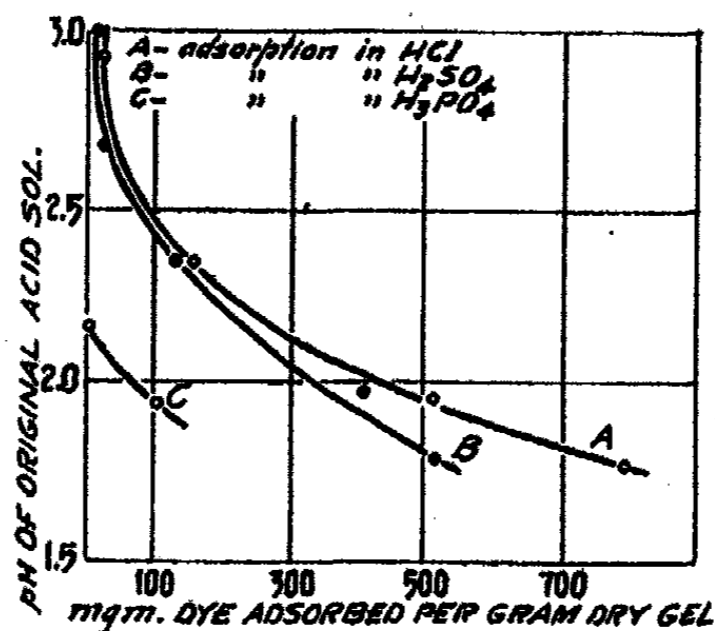


FIG. 5

Adsorption of Orange II by Iron Gel in the presence of HCl, H₂SO₄ and H₃PO₄.

TABLE XVIII

The Adsorption of Orange II by Iron Gel in the Presence of three different acids under the same pH

| pH of acid sol. before dye added | Mgm. of dye adsorbed per gm of dry gel | | |
|-------------------------------------|----------------------------------------|--------------------------------|--------------------------------|
| | HCl | H ₂ SO ₄ | H ₃ PO ₄ |
| 2.95 | 8 | 8 | 00 |
| 2.66 | 28 | 15 | 00 |
| 2.33 | 143 | 138 | 00 |
| 2.01 | 440 | 417 | 30 |
| 1.94 | 540 | 500 | 102 |

It is shown here that in their adsorption effects with iron gel, HCl and H₂SO₄ are very much alike and H₃PO₄ has cut out the adsorption entirely except at a very low pH. Fig. 5 shows these data plotted. The results with chromium gel are very similar; these are shown in the following table and in Fig. 6.

It is apparent that hydrochloric and sulphuric acids have almost the same effect again except at a very low pH, and phosphoric acid has very greatly reduced the adsorption. The adsorption in the presence of phosphoric acid passes through a minimum. This result is explained in the theory of this reaction which is developed in the latter part of this paper. With aluminum gel the results are similar.

TABLE XIX
The Adsorption of Orange II by Chromium Gel in the Presence of three different acids under the same pH

| pH of acid sol. before dye added | Mgm. of dye ads. per gm. of dry gel. | | |
|-------------------------------------|--------------------------------------|--------------------------------|--------------------------------|
| | HCl | H ₂ SO ₄ | H ₃ PO ₄ |
| 2.95 | 24 | 24 | 5 |
| 2.66 | 41 | 35 | 4 |
| 2.33 | 155 | 150 | 00 |
| 2.01 | 475 | 346 | 15 |
| 1.94 | 500 | 390 | 88 |

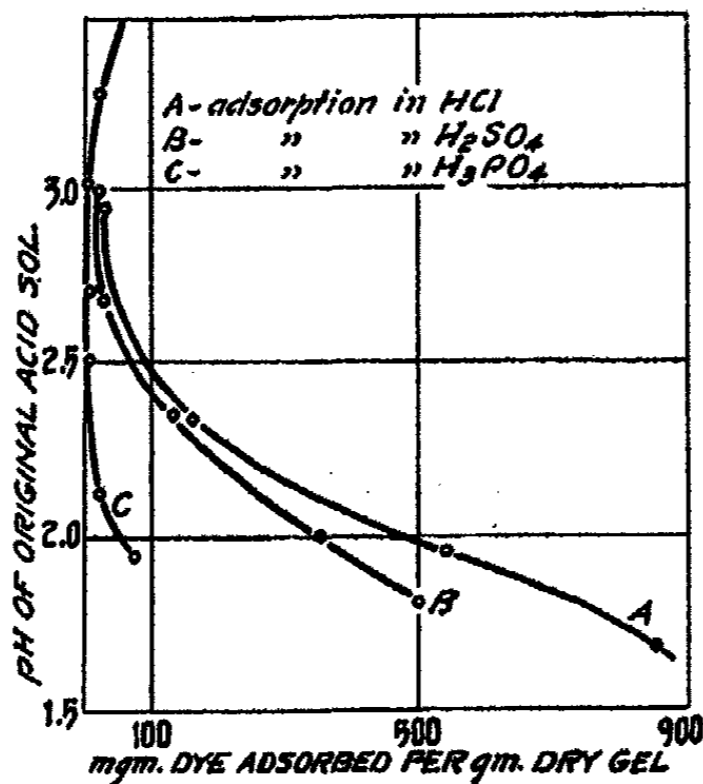


FIG. 6
Adsorption of Orange II by Chromium Gel in the presence of HCl, H₂SO₄, and H₃PO₄.

TABLE XX
The Adsorption of Orange II by Aluminum Gel in the Presence of three different acids under the same pH

| pH of acids sol. before dye added | Mgm of dye ads. per gm. of dry gel. | | |
|--------------------------------------|-------------------------------------|--------------------------------|--------------------------------|
| | HCl | H ₂ SO ₄ | H ₃ PO ₄ |
| 2.95 | 90 | 95 | 15 |
| 2.66 | 95 | 96 | 1 |
| 2.33 | 222 | 215 | 25 |
| 2.01 | 560 | 540 | 160 |
| 1.94 | 650 | 620 | 363 |

These results are brought out more clearly in Fig. 7. Here again hydrochloric acid seems to offer the best adsorption medium with sulphuric acid very nearly equal to it and with phosphoric acid there is very little adsorption at all. At a very low pH the amount of dye adsorbed with phosphoric acid present increases very rapidly.

Since the control of the pH has been shown to be a very important factor it was carefully followed in all the stages of the above experiment. The results are given separately for each acid.

When the gel was added to the dye solutions it was mixed with a considerable quantity of water, (47 gms. water plus 1 gram gel). The dilution and the pH of this water had an effect upon the final pH of the bath, but since this was constant in every case it does not enter into the comparison of the effects of the acids. The water with iron gel had a pH of 7.5, that with aluminum 8.36 and with chromium 8.35.

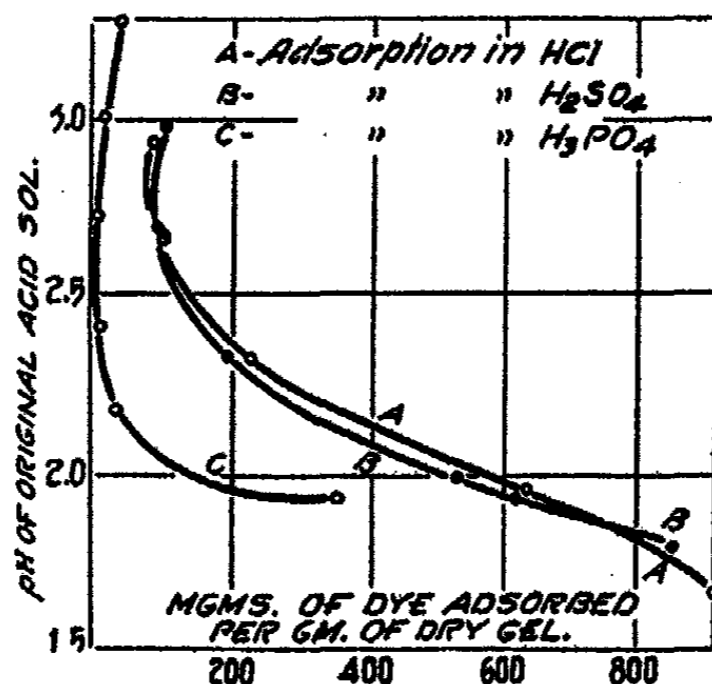


Fig. 7

Adsorption of Orange II by Aluminum Gel in the Presence of HCl, H₂SO₄ and H₃PO₄.

TABLE XXI

The pH Changes during the Adsorption of Orange II in the Presence of HCl

| pH of original acid solution before dye added | pH of solution after adding 1 gm of dye to 200 cc sol | pH of bath after equilibrium was reached | | |
|-----------------------------------------------|-------------------------------------------------------|------------------------------------------|--------|--------|
| | | Al gel | Cr gel | Fe gel |
| 2.95 | 6.4 | 6.63 | 6.91 | 6.74 |
| 2.66 | 6.0 | 5.85 | 6.93 | 6.34 |
| 2.33 | x | 5.48 | 6.27 | 6.12 |
| 1.96 | x | 5.24 | 5.85 | 5.10 |
| 1.65 | x | 3.82 | 2.47 | — |

In the solutions marked x the pH could not be taken due to the dye precipitating out on the electrode.

TABLE XXI

The pH Changes during the Adsorption of Orange II in the Presence of Sulphuric Acid.

| pH of original acid solution before dye added | pH of solution after adding 1 gm of dye to 200 cc sol. | pH of bath after equilibrium was reached | | |
|-----------------------------------------------|--------------------------------------------------------|------------------------------------------|--------|--------|
| | | Al gel | Cr gel | Fe gel |
| 2.98 | 6.4 | 7.12 | 7.14 | 6.30 |
| 2.69 | 6.3 | 6.71 | 7.13 | 5.85 |
| 2.38 | x | 6.08 | 6.40 | 5.48 |
| 2.01 | x | — | 5.58 | 4.94 |
| 1.79 | x | 3.82 | 4.72 | — |

TABLE XXII
The pH Changes during the Adsorption of Orange II in the Presence of Phosphoric Acid

| pH of original acid solution before dye added | pH after adding 1 gm dye to 200 cc solution | pH of adsorption bath after equilibrium was reached | | |
|-----------------------------------------------|---------------------------------------------|-----------------------------------------------------|--------|--------|
| | | Al gel | Cr gel | Fe gel |
| 3.29 | 6.66 | 7.40 | 7.20 | 6.47 |
| 3.01 | 6.59 | 7.13 | 7.10 | 6.32 |
| 2.74 | 4.9 | 7.05 | 7.00 | 6.28 |
| 2.42 | x | 7.46 | 6.10 | 6.20 |
| 2.18 | x | 5.10 | 5.88 | 4.81 |
| 1.94 | x | 3.20 | 2.57 | 2.08 |

The increase in pH of the solution on mixing the dye with the acid is due to the formation of the acid dye. It was the formation of this acid dye that made it impossible to determine the pH of the solutions marked x, for when this material is present in large quantities it precipitates on the electrode.

It will be noticed in the above data that when the final pH of the bath was in general below 6.5 with hydrochloric and sulphuric acids quite a large amount of dye was adsorbed. This point varies, of course, with the different gels. But with phosphoric acid before any quantity of adsorption could be obtained the final pH of the bath was lowered to 3.2 for aluminum gel, 2.57 for chromium gel and 2.07 for iron gel.

A few drops of chromium, aluminum, and ferric chlorides were added to the respective phosphoric acid dye baths which had given little or no adsorption. A precipitate of the metal dye compound immediately resulted. This seemed to indicate that one of the conditions necessary to get the dye removed or adsorbed was to have the metal present in an ionizable compound. Had the ions been present before, adsorption would have resulted. At almost any pH value when sulphuric or hydrochloric acid is in the presence of aluminum, iron, or chromium gel, metallic ions will be liberated because of the formation of a soluble sulfate or chloride. With phosphoric acid reacting with the gel, aluminum, iron or chromium phosphate would form, all of which are relatively insoluble except in more concentrated acid solutions. If this theory is true, that the liberation of the metallic ion is necessary in order for it to react with the dye and form the metal-dye compound, then we should find, at the pH values where adsorption was obtained with phosphoric acid, that iron phosphate is soluble and will yield ferric ions in solution. In order to determine this the following experiment was performed.

Ferric phosphate was prepared by treating potassium dihydrogen phosphate with ferric chloride. A white flocculent precipitate was obtained which became curdy on boiling. To equal amounts of this were added varying amounts of .2N phosphoric acid. This was boiled and let stand for a few hours. In some of the tubes it could be seen that some of the ferric phosphate had dissolved, but some white precipitate still remained in all of them. The pH values of the solutions were determined and they were tested for ferric

ions with potassium sulfo-cyanate. At a pH of 6.88 no ferric ions were present. At 2.40 there was a faint test for ferric ions, lower than this at pH 2.077 and 2.029 the number of ions in solution increased greatly. This can be tested qualitatively by adding KCNS to ferric chloride and then adding Na_2HPO_4 . Under these conditions the color will disappear. If phosphoric acid is added, the characteristic red color of ferric ions will reappear due to the ferric phosphate which was first formed dissolving again.

In order to confirm this and have conditions exactly the same as in the dye adsorption experiment, iron gel was mixed with phosphoric acid solutions of various concentrations and subjected to the same conditions under which the adsorption of the dye was carried out. Results were obtained confirming those given above. With solutions of pH above 4.00 no ferric ions were found in solution. Below this the lower the pH the more ions there were present.

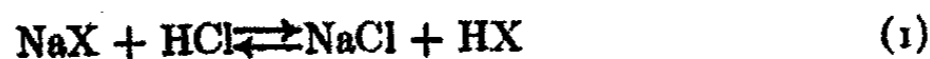
Aluminum phosphate was prepared by treating a solution of potassium monohydrogen phosphate with aluminum chloride. This was treated in the same manner as the iron. A total of seven solutions were used. In these the number of aluminum ions present seemed to pass through a minimum at pH of 5.6 above this number of ions present increased and below this the lower the pH the greater was the number of ions present. It is believed that this is due to the amphoteric nature of the aluminum. Referring back to Table XX and Table XXIII we find that the amount of Orange II adsorbed passes through a minimum when the final pH of the bath corresponds very closely to this.

Chromium phosphate was prepared in exactly the same manner as iron phosphate and a similar experiment tried. At a pH of 6.0 there was a trace of chromium ions in solution but they did not appear in an appreciable amount until a pH of 2.8 was reached, lower than this the amount present increased rapidly. Referring back to Tables XIX and XXIII, it will be noticed that with chromium gel a small amount of dye was adsorbed in the presence of phosphoric acid at a pH of 5.6 but the first adsorption of a large amount of dye was at a pH of 2.6.

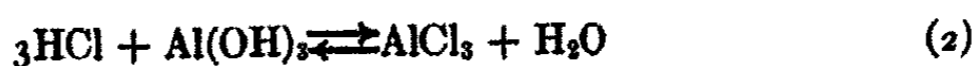
In every case the adsorption of the dye checks very closely with the amount of metal passing into solution in the form of ions. Here we believe is the explanation of the effect of the phosphate radical on the adsorption of an acid dye. The amount of dye removed depends upon the number of metal-ions there are in solution to react and form the metal-dye compound. Hydrochloric and sulphuric acids react with the gels, form soluble salts and furnish the metal ions to the solution. The more acid there is present the more metal ions there will be in solution, hence we find the greater adsorption of the dye at the lower pH. With phosphoric acid, however, reacting with the gel relatively insoluble salts are formed and no ions are furnished to the solution until the acidity is of such concentration that it dissolves these salts. As was shown the solubility of these phosphates vary, iron being the most insoluble.

The series of reactions through which this process of dyeing the mordant, goes are thought to be as follows: For simplicity let x represent the dye radical.

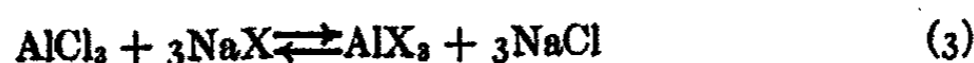
Gordon and Marker have shown that the compound formed by the dye with the metals is AlX_3 , FeX_3 and CrX_3 . Aluminum gel and hydrochloric acid are used as an illustration.



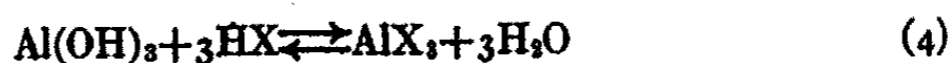
That this reaction takes place and forms the weaker acid HX is shown by the great increase in pH when Orange II is added to an acid solution. Data illustrating this are given in Tables XXI-XXIII.



This reaction was proven by taking various mixtures of the acid and gel and testing for the ions formed.

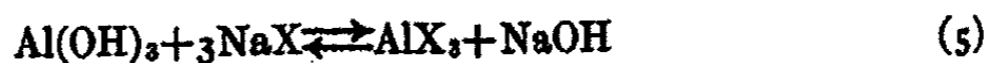


The salt AlX_3 is relatively insoluble and is thus removed from the field of action. This reaction has been illustrated by adding crystals of aluminum, iron and chromium chlorides to a water solution of Orange II. In every case an immediate precipitate results. It is believed that most of the metal-dye compound is formed by this reaction. A small fraction may be formed by the reaction of the dye acid and the gel but this is highly improbable since the base is extremely weak and the acid is relatively weak.

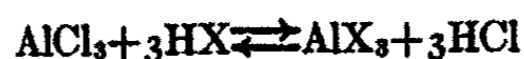


If this is the essential reaction then phosphoric acid should assist the dyeing just as effectively as sulphuric or hydrochloric acids, because with phosphoric acid the dye acid, HX, is formed just as in the other two cases as the data in Table XXIII show.

If no acid is present some small amount of the metal dye salt may be formed due to the slight ionization of aluminum hydroxide.



There is also the possibility that some of the dye acid formed reacts with the $AlCl_3$ formed by reaction (2).



However the evidence seems to indicate that the essential reaction for the formation of the metal-dye compound is reaction (3). On the basis of this we can explain the very sudden increases in adsorption of Orange II at a low pH which were noted by Gordon and Marker. They found that the adsorption of Orange II increased steadily until a certain relatively low pH was reached; at this point further addition of acid caused very rapid increase in the adsorption. We explain this point by claiming that it occurs at the hydrogen ion concentration where enough acid has been added to shift reaction (1) as far as possible to the right. Any more acid added would react directly with the gel and proceed through reactions (2) and (3).

With sulphuric acid the reactions given above would be of the same nature as with hydrochloric acid.

With phosphoric acid, reaction (1) is the same as with hydrochloric. But in reaction (2) there would be formed either $\text{Al}(\text{H}_2\text{PO}_4)_3$, $\text{Al}_2(\text{HPO}_4)_3$ or AlPO_4 . Since there is a large amount of gel present and only a small amount of acid it is believed that the major compound would be AlPO_4 . This compound was shown to be relatively insoluble and corresponding salts of chromium and iron still more insoluble. The formation of this insoluble product in reaction (2) would prevent reaction (3) from taking place and hence would prevent adsorption, by this reaction taking place. This is borne out by the experimental data given above. Aluminum phosphate was found to be slightly soluble under all the conditions used and some adsorption of the dye was found in all cases. The pH values at which chromium gel gave adsorption of dye in the presence of phosphate were found to correspond with those at which chromium phosphate yielded chromium ions to the solution. And finally, it was found that iron gel in the presence of phosphates adsorbed dye at only a very low pH value. This corresponded to the point at which iron phosphate yielded ferric ions to the solution.

The experimental facts seem to indicate that in order to have an acid dye removed from solution by a gel, in any large quantity, the metal ion must be free. This is accomplished by adding sulphuric or hydrochloric acids which react with the gels to form soluble salts. Phosphates decrease the adsorption because of the formation of difficultly soluble salts with the gels.

Summary of Experimental Results

I. The presence of .05 normal potassium dihydrogen phosphate greatly decreased the adsorption of an acid dye with aluminum gel and iron gel.

II. Using H_2PO_4 solution in the dye bath the adsorption of Orange II was very much decreased with aluminum gel and cut out entirely with iron gel except at a very low pH.

III. Iron gel was allowed to adsorb all of the phosphate from .01N KH_2PO_4 and .012N H_2PO_4 , then Orange II dye was added. No dye was adsorbed.

IV. Iron and aluminum gels were allowed to adsorb dye from a .5 per cent solution of Orange II at pH values varied with KOH and H_2SO_4 . Potassium acid phosphate was then added. Most of the dye was released and the phosphate adsorbed.

V. Iron gel was allowed to remain with dye solutions in .05N potassium acid phosphate for a period of six months. Even at the end of this period no dye was adsorbed.

VI. Iron and aluminum gels were allowed to reach adsorption equilibrium with .05N KH_2PO_4 . The gels were removed, and ground in a mortar then put back into the solutions. There was an increase in adsorption in all solutions used.

VII. The adsorption of Orange II by iron, aluminum, and chromium gels was tried with the following results.

- Aluminum gel: High adsorption of dye with HCl and H₂SO₄.
Low adsorption of dye with H₃PO₄.
- Chromium gel: High adsorption of dye with HCl and H₂SO₄.
Very low adsorption of dye with H₃PO₄.
- Iron gel: High adsorption of dye with HCl and H₂SO₄.
No adsorption of dye with H₃PO₄ except at a very low pH value.

The order of increasing adsorptive power for Orange II is: iron, chromium, aluminum.

VIII. In cases where phosphate is adsorbed from solutions having varying phosphate concentrations the amount adsorbed in the presence of Orange II dye is a straight line function of the amount present.

IX. Chromium, iron, and aluminum as chlorides when mixed with solutions of the sodium salt of Orange II give an immediate precipitate of the respective metal-dye compound.

X. Chromium, iron, and aluminum chlorides dropped into the H₃PO₄ solution from which no dye was adsorbed gave immediate precipitates of the metal-dye compound.

XI. The solubility of aluminum phosphate in phosphate solutions of various hydrogen ion concentrations was found to coincide with the adsorption curve of Orange II by aluminum gel in phosphate solutions.

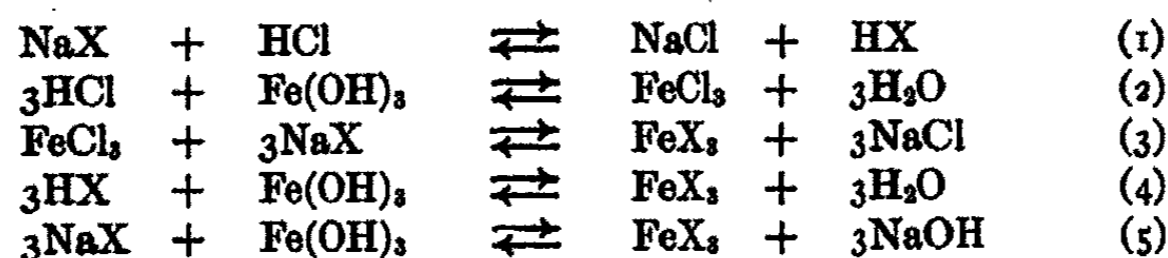
Iron phosphate was found to be soluble at the same pH at which the iron gel adsorbed Orange II.

Chromium phosphate was also found to be soluble in phosphate solutions at the same pH where adsorption of Orange II was found.

Conclusions

The decrease in the adsorption of an acid dye, Orange II, by iron, aluminum and chromium gels (mordants) in the presence of phosphates is not due to any effect of the phosphate radical upon the dye or the solution. It is due to the phosphate forming a relatively insoluble compound with the gels, hence not furnishing any metal ions to react with the dye and form the metal-dye compound which is the cause of adsorption. At high hydrogen ion concentration adsorption takes place because the metal phosphate becomes soluble. The reactions supposed to take place during the adsorption of an acid dye Orange II by an inorganic gel are best expressed in the following equations:

Let x represent the dye radical and using iron gel with a hydrochloric acid solution of the dye for an example:—



It is postulated that most of the adsorption is due to reaction (3). Some little may be due to reactions (4) and (5).

Sulphuric acid acts very similar to hydrochloric in these reactions.

Phosphoric acid acts in reaction (1) similar to hydrochloric. In reaction (2) phosphoric acid forms an insoluble iron phosphate thus preventing reaction (3) from taking place and no adsorption results unless the solution is made sufficiently acid to dissolve the iron phosphate.

Aluminum and chromium gels act similar to iron.

THE EFFECT OF NEUTRAL SALTS ON CERTAIN CATALYTIC DECOMPOSITIONS*

BY C. CLEMENT FRENCH

Much experimental material is available on the velocity of reaction of compounds subject to catalytic decomposition by the hydrogen ion and on the effect of neutral salts in such reactions. Similar studies in cases where the catalyst is the hydroxyl or other ion are not so numerous. With the idea of contributing more experimental data of a comparatively high degree of accuracy to the field of neutral salt action in homogeneous catalysis, this work has been undertaken.

Two reactions were investigated: 1. The decomposition of hydrogen peroxide, catalyzed by the iodine ion. 2. The decomposition of nitroso-triacetone-amine, catalyzed by the hydroxyl ion, each in the presence of various neutral salts.

It is well known that hydrogen peroxide is completely decomposed by solutions of soluble acid-free iodides, the concentration of the iodide or iodine ion remaining constant during the reaction. Walton,¹ from a careful study of the velocity of decomposition of hydrogen peroxide with sodium, potassium and ammonium iodides, has shown the reaction to be of the first order and complete. He further showed that up to concentration of the iodides of about 0.04 N, the reaction appeared to be proportional to the concentration of the iodide ion, and is independent of the concentration of the water. Consequently, this is a reaction which careful study has shown to be an ionic catalysis and in which the effect of neutral salts could be studied on catalysis by an ion other than the hydrogen ion.

Walton has reported only one result on the reaction velocity with each of the following salts: potassium chloride, sodium chloride, potassium sulphate, sodium sulphate, potassium nitrate and potassium chlorate, in a 0.0313 N potassium iodide solution. The effect of the chlorate was negligible, potassium sulphate decreased the velocity slightly while the other salts increased the velocity.

Harned² has studied the effect upon the velocity of this reaction of the addition of potassium, sodium and lithium chlorides, up to concentrations of 3 N, in solutions of 0.02 N and 0.03 N potassium iodide.

Nitroso-triacetone-amine in the presence of the hydroxyl ion changes into phorone, nitrogen and water according to the following equation:



* Contribution from the John Harrison Laboratory of Chemistry of the University of Pennsylvania.

¹ Walton: *Z. physik. Chem.*, **47**, 185 (1904).

² Harned: *J. Am. Chem. Soc.*, **40**, 1461 (1918).

This reaction was discovered by Heintz¹ and has been carefully studied by F. Francis² and his co-workers, who showed it to be a simple first order reaction, catalyzed by the hydroxyl ion. At hydroxyl ion concentrations above 0.05 N, the reaction mechanism appears to change since the monomolecular law which holds at lower hydroxyl ion concentrations fails to hold at these higher catalyst concentrations. More recently, this reaction has been investigated by Brønsted and King³ in connection with secondary kinetic salt effect, and by Kilpatrick⁴ in studying catalysis in buffer solutions. Brønsted and King report the effect of sodium chloride in concentrations up to 0.2 N on the velocity at 15°C, and Kilpatrick the effect of sodium chloride up to about the same concentration on the velocity at various temperatures.

Experimental Methods

Materials:—The action of the following salts was investigated:

1. Chlorides of potassium, sodium, lithium, barium, strontium, calcium and magnesium.
2. Sulphates of potassium, sodium, lithium and magnesium.
3. Bromides of potassium and sodium.
4. Potassium iodide.

All salts were of the best grade of analyzed chemicals obtainable. In all cases where there was no danger of decomposition on heating, the salts were ground and dried by careful heating. After drying, all salts were tested for neutrality. A sample of the salt was dissolved in 50 cc. of distilled water and a few drops of indicator added. The addition of a drop of dilute sodium hydroxide solution in every case gave a sharp color change.

The chlorides of lithium, magnesium and calcium were used in solution. The solutions of the first two were made by adding the salts to redistilled water in quantity nearly sufficient to make a saturated solution at room temperature. It was found that this method could not be employed with calcium chloride. In this case, the analyzed salt was added to redistilled water almost to saturation. The solution was then filtered and a slight excess of hydrochloric acid added to overcome the original alkaline reaction of the solution. Precipitated calcium carbonate was then added in excess to the boiling solution, and the solution filtered while warm. After standing over night, the crystals of calcium chloride were filtered, sucked free of mother liquor, and dissolved in redistilled water, making the final solution as used. The solutions were analyzed by precipitating the chloride ion with silver ion in acid solution, and weighing the silver chloride. As a check, the specific gravity of each solution was determined with the Westphal Balance, and the salt content determined from the Tables of Landolt-Börnstein.

A 3 per cent solution of hydrogen peroxide was used. It contained a trace of acid, but as the maximum concentration used was 4 cc. of this solution in

¹ Heintz: *Ann.* 187, 250 (1877).

² Clibbens and Francis: *J. Chem. Soc.*, 101, 2358 (1912); Francis and Geake: 103, 1722 (1913); Francis, Geake and Roche: 107, 1651 (1915).

³ Brønsted and King: *J. Am. Chem. Soc.*, 47, 2523 (1925).

⁴ Kilpatrick: *J. Am. Chem. Soc.*, 48, 2091 (1926).

100 cc. total volume of solution, the amount of acid present in the final solution was negligible. That this was true was shown by the fact that neutral potassium iodide liberated but a trace of iodine when added to it.

Nitroso-triacetone-amine as purchased was recrystallized by dissolving in the minimum of alcohol at 50°C and precipitating by the addition of a little warm water. The product thus obtained was pressed dry. It was a pale yellow solid, melting at 72°C.

Standard 0.1 N potassium hydroxide solution was made by diluting a nearly saturated solution of potassium hydroxide from which the carbonate had been removed by a slight excess of barium hydroxide. While the standard potassium hydroxide solution contained traces of barium hydroxide, the amount present was almost beyond detection, as in the original solution only a trace was present. The standard alkali solution was analyzed by titration with 0.1 N hydrochloric acid solution which had been standardized gravimetrically. The alkali solution was preserved in a large bottle fitted with soda-lime tubes.

Apparatus:—All measurements were made at $25 \pm 0.01^\circ\text{C}$. The thermostat was rather large, containing over 400 liters of water. The heating was controlled by a large grid-shaped thermo-regulator, filled with mercury and having a surface of over 2000 sq. cm. Variations in the temperature could not be detected on a Beckmann thermometer for periods of several days, so the deviation from 25° during a measurement was probably less than 0.01°C .

The decomposition of hydrogen peroxide is accompanied by the evolution of oxygen and that of nitroso-triacetone-amine by the evolution of nitrogen. Hence the velocity of each of these reactions can be determined by measuring the volume of the gas evolved at various time intervals. Walton and Francis¹ both obtained sufficient agitation by rapid shaking of the reaction vessel. Brönsted and King² also used this method. Harned, and more recently Kilpatrick,³ used the stirring method for the agitation of the solution. In either case, the important point is "to agitate the solution to such an extent that the gas is registered on the volume-measuring apparatus as soon as it is produced in the solution."⁴ In this work, the solution was agitated by a rapidly revolving glass stirrer, sealed off from the outside by a mercury seal.

The reaction vessel is shown in Fig. 1. A is a 500 cc. Pyrex Erlenmeyer flask, in the bottom of which three openings have been made. The tube B, sealed in through the first opening, is a 2 mm. capillary through which water or salt solution was added. The upper end of this tube was connected by a ground glass slip-on joint to the filling cup C. The tube D, sealed into the flask through the trap E, led to the gas volume burette. The latter was similar to that used by Walton,⁵ and contained water. The gas burette was sur-

¹ Walton: *Z. physik. Chem.*, 47, 185 (1904); Clibbens and Francis: *J. Chem. Soc.*, 101, 2358 (1912).

² Brönsted and King: *J. Am. Chem. Soc.*, 47, 2523 (1925).

³ Harned: *J. Am. Chem. Soc.*, 40, 1461 (1918). Kilpatrick: *J. Am. Chem. Soc.*, 48, 2091 (1926).

⁴ Harned: *J. Am. Chem. Soc.*, 40, 1461 (1918).

⁵ Walton: *Z. physik. Chem.*, 47, 185 (1904).

rounded by a water jacket, maintained at a temperature of 25° by pumping water from the thermostat through it. To the flask at the third opening was sealed the tube F, of a diameter sufficient to permit the withdrawing of the stirrer. The larger concentric tube G, forming a trough for the mercury seal, was sealed to the tube F. To the stirrer shaft was sealed the tube, H-H, of a proper diameter to dip down into the mercury reservoir as shown. The stirrer shaft J revolved in two close fitting brass tubes, K-K, which in turn were clamped firmly in position. The pulley L was securely fastened to the glass tubing M, which in turn was sealed to the stirrer shaft. Since the stirrer was rotated at a high rate of speed, it was necessary that the shaft be carefully centered to prevent splashing of the mercury and consequent gas leakage.

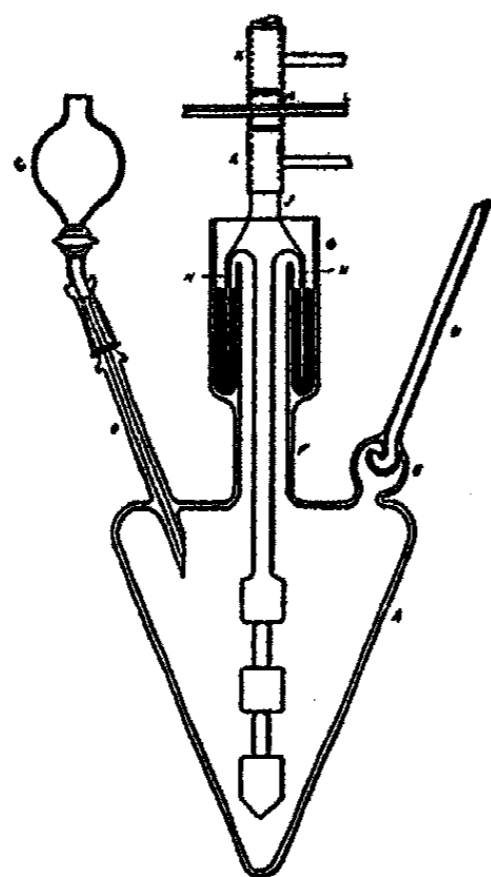


FIG. 1

The following procedure was adopted in making the measurements with hydrogen peroxide. The reaction vessel was first carefully washed with water and alcohol, and dried in a current of air. The filling cup C was then attached and secured by small rubber bands fastened over the glass hooks at the joint. Then a weighed quantity of salt was added through the tube F, or if a salt solution was being used, through the filling cup. Then to this was added the calculated quantity of water, together with 4 cc. of the 3 per cent hydrogen peroxide solution. The apparatus was placed in the thermostat bath and the contents of the vessel stirred until the salt had

dissolved and the solution had come to the temperature of the bath. The stirrer was then removed and the proper quantity of solid potassium iodide, weighed out and wrapped in a small piece of filter paper, was dropped in. The stirrer was replaced, the gas outlet tube D fastened to the gas burette by a piece of tight-fitting rubber tubing and mercury added to make the seal. The stirrer was then rotated and when the potassium iodide had dissolved and a steady evolution of oxygen was secured, readings of the gas burette were begun. Readings were taken at convenient intervals until the decomposition was over 75 per cent complete. After that the reaction was allowed to proceed to completion and the final volume recorded.

In the work with nitroso-triacetone-amine, essentially the same procedure was followed, 0.15 grams of the nitrosamine, together with the calculated quantity of water and salt or standard salt solution, were placed in the reaction vessel. The whole was then stirred in the thermostat until solution was obtained at the temperature of the bath. As the nitrosamine dissolves very slowly in water at 25° , care had to be taken that sufficient time was allowed for its complete solution. When this was accomplished, the standard alkali solution was added through the filling cup, the delivery tube attached to the

gas burette as above and readings begun when about 2 cc. of nitrogen had been evolved. When sufficient readings had been obtained, the stirrer was stopped because of the long time necessary for the completion of the reaction. After standing for over 24 hours, the solution was again stirred for 30 minutes and the final volume read on the gas burette. Readings of the volume were made to 0.05 cc. In the work with hydrogen peroxide, a total volume of 100 cc. was used: with the nitroso-triacetone-amine, 200 cc.

**Effect of Various Salts on the Decomposition of Hydrogen Peroxides,
catalyzed by the Iodine Ion**

A number of preliminary experiments were necessary. Hydrogen peroxide solution is slowly decomposed by sharp glass edges and by ground glass. In order to determine the extent of this decomposition, as well as to make sure

TABLE I
Decomposition of Hydrogen Peroxide in Absence of Potassium Iodide

| Exp. No. | Substance in Reaction Vessel | Time, hours | Cc. of O ₂ evolved |
|----------|------------------------------------------------------------------------------------------------------------|-------------|-------------------------------|
| 1 | 4 cc. H ₂ O ₂ + 96 cc. H ₂ O | 2.0 | 0.00 |
| 2 | 4 cc. H ₂ O ₂ + 96 cc. H ₂ O + filter paper | 2.0 | 0.00 |
| | | 3.0 | 0.05 |
| 3 | 4 cc. H ₂ O ₂ + filter paper + 96 cc. KBr 3N | 1.0 | 3.3 |
| | | 2.0 | 5.3 |
| | | 3.0 | 8.45 |
| 4 | 4 cc. H ₂ O ₂ + filter paper + 96 cc. NaBr 3N | 0.5 | 5.4 |
| | | 1.5 | 13.9 |
| | | 2.0 | 17.4 |
| 5 | 4 cc. H ₂ O ₂ + filter paper + 96 cc. CaCl ₂ 1.5N | 0.5 | 2.1 |
| | | 1.0 | 3.95 |
| | | 2.0 | 6.8 |
| 6 | 4 cc. H ₂ O ₂ + filter paper + 96 cc. BaCl ₂ 1.5N | 0.5 | 0.45 |
| | | 1.0 | 0.85 |
| | | 2.5 | 1.7 |
| 7 | 4 cc. H ₂ O ₂ + filter paper + 96 cc. SrCl ₂ 1.5N | 0.75 | 0.4 |
| | | 1.5 | 1.0 |
| | | 3.0 | 1.6 |
| 8 | 4 cc. H ₂ O ₂ + filter paper + 96 cc. MgCl ₂ 1.5N | 1.0 | 0.45 |
| | | 2.0 | 0.45 |
| 9 | 4 cc. H ₂ O ₂ + filter paper + 96 cc. Na ₂ SO ₄ 3N | 3.0 | 0.00 |
| 10 | 4 cc. H ₂ O ₂ + filter paper + 96 cc. K ₂ SO ₄ 1.25N | 3.0 | 0.00 |
| 11 | 4 cc. H ₂ O ₂ + filter paper + 96 cc. Li ₂ SO ₄ 3N | 3.0 | 0.00 |
| 12 | 4 cc. H ₂ O ₂ + filter paper + 96 cc. MgSO ₄ 3N | 3.0 | 0.00 |
| A | 5 cc. H ₂ O ₂ + 20 cc. KCl 3N | 2.0 | 0.10 |
| | | 3.0 | 0.20 |
| B | 5 cc. H ₂ O ₂ + 20 cc. NaCl 3N + filter paper | 2.0 | 0.25 |
| | | 3.0 | 0.40 |

that the apparatus under the conditions of the experiment was gas-tight, preliminary runs were made with the hydrogen peroxide present in the vessel, but without the catalyst. It was also necessary to determine whether the filter paper in which the potassium iodide was added, had any effect on the rate of decomposition. Finally, runs were made in the absence of potassium iodide with each of the salts whose effect was to be studied, in order to ascertain whether they alone produced an appreciable evolution of oxygen; and to determine the rate of such evolution if sufficient to make a future correction necessary. These results are summarized in Table I.

Experiments A and B in the above table are taken from the data of Harned¹ and are inserted here to emphasize the relation between the various salts and the magnitude of the effect produced by them in the absence of potassium iodide. The above results show without question that any decomposition due to the apparatus, stirrer or filter paper is negligible. The presence of concentrated solutions of bromides and chlorides does cause a slow decomposition of hydrogen peroxide. Engler and Nasse and Schöne² have reported that concentrated chloride and bromide solutions slowly decompose hydrogen peroxide, and that of the two the action of the bromide is the more vigorous. The results shown above confirm this. The magnitude of the corrections will be considered later.

The velocity constants are calculated according to the equation of the first order,

$$K = 2.303/t \log_{10}(V_{\infty} - V_0)/(V_{\infty} - V_t)$$

where K is the velocity constant, t the time in minutes, V_{∞} the final reading of the gas burette, V_0 the reading at time $t = 0$, and V_t the reading at any time t . In most cases, the calculation of K in this manner gave values of good constancy. In a few cases, the first one or two values of K showed a regular change, and in these cases the values were discarded and the next reading taken as the starting point. This recalculation in most cases gave a series of values for K of a satisfactory degree of constancy. If not, the measurements were repeated with freshly prepared solutions. In Table II, two complete series of constants are given to show the degree of constancy obtainable.

The maximum variation from the mean in the first series is 1.5 per cent, and in the second 1.3 per cent. The maximum variation from the mean in any of the runs giving accepted results was never greater than 2.5 per cent. Duplication of the series with barium, strontium and calcium chlorides, as well as the repetition of various check points with the other salts showed that the mean value of K could be reproduced in two completely different experiments to within 1.5 per cent. This compares favorably with the constancy and reproducibility reported by Francis³ and by Walton⁴ on measurements of this

¹ Harned: *J. Am. Chem. Soc.*, **40**, 1461 (1918).

² Engler and Nasse: *Ann.*, **154**, 231 (1870); Schöne: **195**, 228 (1879).

³ Clibbens and Francis: *J. Chem. Soc.*, **101**, 2358 (1912).

⁴ Walton: *Z. physik. Chem.*, **47**, 185 (1904).

TABLE II
Velocity of Decomposition of Hydrogen Peroxide Solution

| Time Seconds | Gasometer Reading | K |
|--------------------------------------------------------------------|----------------------|--------|
| 0 | 7.95 | |
| 190 | 11.15 | 0.0273 |
| 555 | 16.55 | 0.0271 |
| 730 | 18.95 | 0.0274 |
| 910 | 21.05 | 0.0272 |
| 1230 | 24.40 | 0.0270 |
| 1545 | 27.25 | 0.0270 |
| 2475 | 33.70 | 0.0265 |
| 3085 | 36.85 | 0.0266 |
| ∞ | 46.70 | |
| Mean K = | | 0.0270 |
| 2. Catalyst 0.02N Potassium Iodide. Presence of N Barium Chloride. | | |
| 0 | 10.35 | |
| 100 | 13.15 | 0.0532 |
| 270 | 17.45 | 0.0538 |
| 370 | 19.50 | 0.0526 |
| 860 | 27.85 | 0.0526 |
| 1005 | 29.90 | 0.0535 |
| 1365 | 33.65 | 0.0537 |
| 1670 | 36.00 | 0.0538 |
| 2050 | 38.00 | 0.0530 |
| ∞ | 43.40 | |
| Mean K = | | 0.0532 |

kind. A further check on the accuracy of the values obtained is found in a comparison of the values for K at a catalyst concentration of 0.02N and in the absence of added salt. While Walton does not report a result for this exact concentration, the value read for it from a curve drawn through K values for concentrations on both sides of 0.02N is 0.0265; Harned¹ reports 0.0275, while the value obtained here is 0.0270. This lies midway between the two other values, and differs from them by about 1.8 per cent, which was found to be about the reproducibility in independent experiments.

Referring now to Table I, it is found that the various neutral salts have very different effects upon hydrogen peroxide in the absence of potassium iodide. The halides have a rapidly decreasing effect in the order iodide, bromide, chloride, while the sulphates show no action. In the case of the

¹ Harned: J. Am. Chem. Soc., 40, 1461 (1918).

chlorides, it is interesting to note that the magnitude of the effect produced in equivalent salt concentrations is quite different with different cations. Since at 25° these decompositions were quite slow, the values obtained for infinity reading of the gas burette would have been of very uncertain quality. Hence

TABLE III
Rate of Decomposition of Hydrogen Peroxide in Absence of Potassium Iodide

| Salt | ΔK per Gram Equivalent of Salt |
|-----------------------------|----------------------------------------|
| NaBr | 0.0016 |
| KBr | 0.0012 |
| CaCl ₂ | 0.0013 |
| BaCl ₂ | 0.0003 |
| SrCl ₂ | 0.0003 |
| MgCl ₂ | 0.0001 |

TABLE IV
Iodide Ion Catalysts of Hydrogen Peroxide in Neutral Salt Solutions
Catalyst 0.02N Potassium Iodide. Temperature 25°C.

| N | Values of $K \times 10^4$ | | | | | | |
|------|---------------------------|--------|-------------------|---------------------------------|--------------------------------|---------------------------------|-------------------|
| | NaBr | KBr | MgSO ₄ | Li ₂ SO ₄ | K ₂ SO ₄ | Na ₂ SO ₄ | MgCl ₂ |
| 0.0 | 270 | 270 | 270 | 270 | 270 | 270 | 270 |
| 0.25 | — | — | — | — | — | — | 297 |
| 0.3 | — | — | — | — | 267 | — | — |
| 0.5 | 292 | — | 306 | 296 | — | 277 ₆ | 348 |
| 0.6 | — | — | — | — | 262* | — | — |
| 0.75 | — | — | — | — | — | — | 392 |
| 0.9 | — | — | — | — | 259 | — | — |
| 1.0 | 322 | 293 | 357 | 313 | — | 287 | 440* |
| 1.25 | — | — | — | — | 257* | — | 491 |
| 1.5 | 356 | 301.5* | 415* | 353 | — | 292* | 550 |
| 1.75 | — | — | — | — | — | — | 620 |
| 1.8 | — | — | — | — | — | 289 | — |
| 2.0 | 404 | 314 | 491 | 384* | — | — | 706 |
| 2.4 | — | — | 554 | — | — | 302 | — |
| 2.5 | 452* | 332 | — | 418 | — | — | — |
| 3.0 | 516 | 344 | 655 | 451 | — | 308 | — |

| N | Values of $K \times 10^4$ | | | | | |
|------|---------------------------|-------------------|-------------------|-------------------|-------------------|--------------------------------------|
| | CaCl ₂ | CaCl ₂ | SrCl ₂ | SrCl ₂ | BaCl ₂ | BaCl ₂ ·2H ₂ O |
| 0.0 | 270 | 270 | 270 | 270 | 270 | 270 |
| 0.25 | 333 | 333 | 313 | — | 346 | 347 |
| 0.5 | 393 | 387 | 351 | 359 | 402 | 401 |
| 0.75 | 455 | 450 | 422 | 431 | 472 | 459 |
| 1.0 | 529 | 516 | 481 | 491 | 532 | 515 |
| 1.25 | 578 | 579 | 553 | 549 | 604 | 598 |
| 1.5 | 671 | 662 | 643 | 631 | 708 | — |

*Mean of two values.

a number of readings were made over a period of three hours or more (only a few of which are listed in Table I) and from these readings, taking a value for the infinity reading such as to give the greatest constancy to the series of K values calculated, the mean value of K for each decomposition was determined. A summary of these results is contained in Table III.

The corrections to the observed values of the rates of decomposition in the presence of potassium iodide and neutral salts would be less than 1 per cent in the cases of barium chloride, strontium chloride and magnesium chloride, hence no correction has been applied in these cases. With sodium and potassium bromides and calcium chlorides, the correction in Table III was used. This was taken as proportional to the salt concentration, since it was found in the pure salt solution that the rate was very nearly proportional to the concentration of salt. Table IV contains the mean corrected values of K. All salt concentrations are in weight normality.

Effect of Various Salts on the Decomposition of Nitrogen-Triacetone-Amine, catalyzed by the Hydroxyl Ion

Brønsted and King¹ have pointed out that carbon dioxide must be excluded from the apparatus and Kilpatrick² worked in an atmosphere of nitrogen, in order to exclude oxygen as well as carbon dioxide, during the course of this reaction. The apparatus as previously described was designed for the hydrogen peroxide reaction, and did not readily permit of operation in an inert gas atmosphere. The purpose of this investigation was not so much to obtain absolute values for the reaction velocity constant as to secure the distribution of the curves caused by the addition of various neutral salts. Recently Åkerlöf³ has measured the velocity of decomposition of diacetone alcohol to acetone in alkali hydroxide-alkali salt solutions. This work affords one of the few exact investigations of a decomposition catalyzed by the hydroxyl ion. It was thought that it would be of interest to compare the distribution of the velocity constant curves for a few salts with each of these reactions, since each is a first order reaction catalyzed by the hydroxyl ion. By working at a temperature lower than that used by Francis,⁴ and at a much lower concentration of hydroxyl ion, the salt effect would be greater for the same salt concentration and consequently the curves for various salts would be more widely distributed.

The error due to any carbon dioxide in the reaction vessel should be fairly constant in all experiments, since the same procedure was followed consistently. The alkali solution was never added until just before the vessel was closed off from the air, and the volume of air space above the liquid was always the same. The results seem to indicate that these assumptions were justified, for quite uniform results were obtained, and the curves for the various salts are reasonably smooth.

¹ Brønsted and King: *J. Am. Chem. Soc.*, **47**, 2523 (1925).

² Kilpatrick: *J. Am. Chem. Soc.*, **48**, 2091 (1926).

³ Åkerlöf: *J. Am. Chem. Soc.*, **48**, 3046 (1926).

⁴ Clibbens and Francis: *J. Chem. Soc.*, **101**, 2358 (1912).

One other point regarding the measurements should be mentioned. Due to the slowness of this decomposition in the presence of salts at fairly high concentrations, the quantity of nitrogen evolved between two readings of the gas burette at ten minute intervals often was not more than 1 cc. An error of 0.05 cc., the limit of accurate reading, would make a much greater variation probable in a series of readings than in the case of the hydrogen peroxide series, where from 7 to 8 cc. were collected during the same time. Consequently, for a given series variations of 3 to 4 per cent from the mean value of K were not uncommon. This was also found by Francis,¹ who reported the variation as about 3 per cent. Table V contains the mean values of K .

TABLE V
Hydroxyl Ion Catalysts of Nitroso-Triacetone-Amine in Neutral Salt Solutions

Catalyst 0.014N Potassium Hydroxide. Temperature 25°C.

| N | Values of $K \times 10^4$ | | | | |
|-----|---------------------------|------|------|-----|-----|
| | KCl | NaCl | LiCl | KBr | KI |
| 0.0 | 143 | 143 | 143 | 143 | 143 |
| 0.5 | 120 | 116 | 105 | 107 | 83 |
| 1.0 | 109 | 100 | 84 | 87 | 57 |
| 1.5 | 98 | — | — | 80 | 46 |
| 2.0 | 93 | 80 | 54 | 65 | 37 |
| 2.5 | 85 | — | — | 54 | 27 |
| 3.0 | 80 | 57 | 33 | 47 | 23 |

The values for K have been calculated as in the previous work with hydrogen peroxide, using the minute as the unit of time. While no very good agreement was expected, the value of K for 0.014N potassium hydroxide in the absence of neutral salt was compared with the value of Francis. Since Francis worked at 30°, and did not record a value for K at the concentration of catalyst used here, it was necessary to secure a value from his results comparable with the value found above. From a curve of his values at varying potassium hydroxide concentrations at 30°C, the value $K = 0.0250$ at 0.014N catalyst concentration was read off. Kilpatrick² has recently determined the temperature coefficients of this reaction between 20°C and 30°C, using sodium hydroxide as the catalyst. He reports $K_{30}/K_{20} = 2.57$. Assuming that $K_{30}/K_{25} = K_{25}/K_{20}$, K_{30}/K_{25} would equal 1.6. With this value of the temperature coefficient, the value of Francis at 30° becomes $K = 0.0156$ at 25°C. The value obtained here for the same catalyst concentration is $K = 0.0143$, a difference of about 8 per cent, which was rather an unexpectedly close agreement.

In addition to the experiments with the salts listed above, a considerable number of runs were made with sodium, potassium and lithium sulphates. The results obtained were most irregular, in spite of repeated efforts to obtain

¹ Clibbens and Francis: *J. Chem. Soc.*, 101, 2358 (1912).

² Kilpatrick: *J. Am. Chem. Soc.*, 48, 2091 (1926).

values which would fall on a smooth curve. In general, sodium sulphate appeared to cause a slight increase in velocity; potassium sulphate a decrease, but not approaching the magnitude of the salts listed above; and lithium sulphate a decrease in velocity approaching in magnitude that caused by sodium chloride. This irregular action with the alkali sulphates agrees with the observations of Francis¹ on the same salts. He also was unable to secure consistent values.

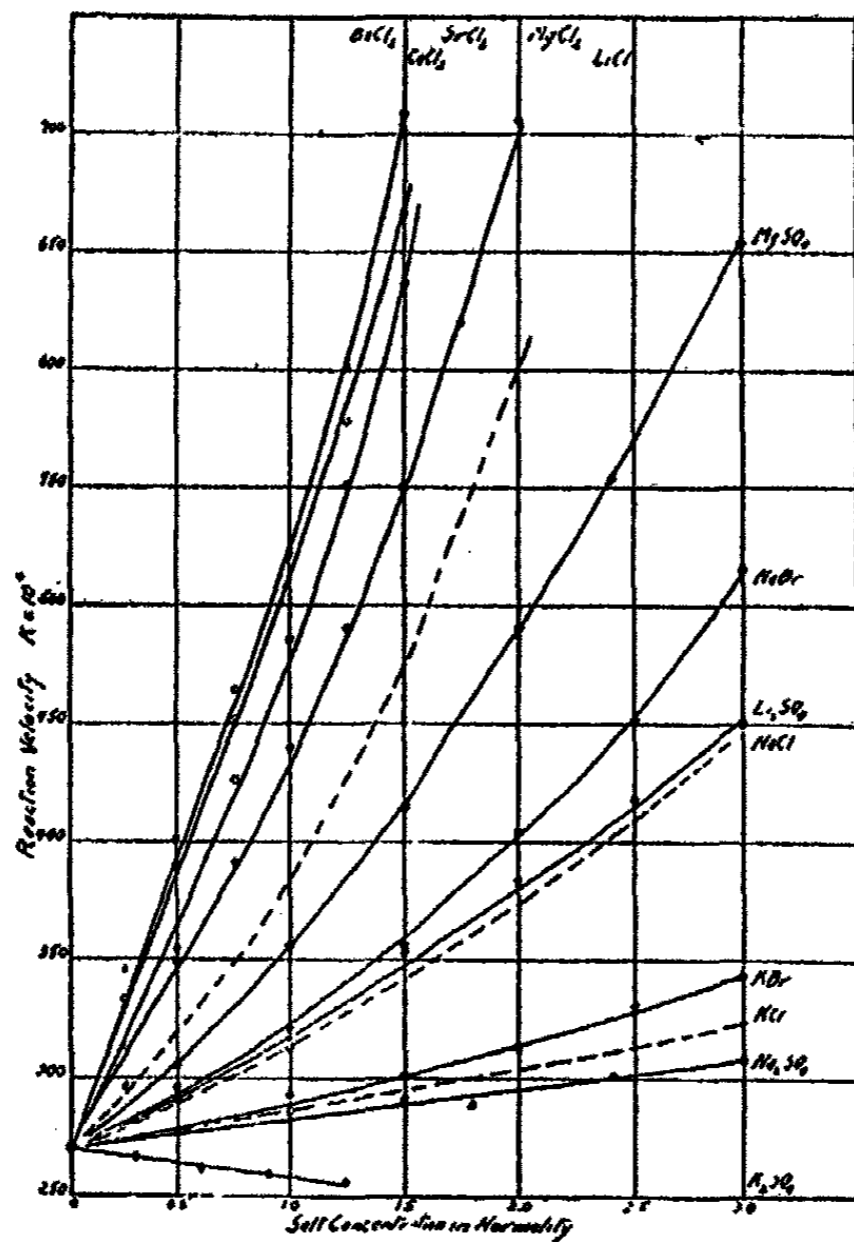


FIG. 2

Curves for the reaction velocity of the decomposition of hydrogen peroxide in neutral solutions of 0.02 *N* potassium iodide and increasing concentration of various salts.

Discussion

1. Hydrogen Peroxide Decomposition.

In Fig. 2, the reaction velocity constant *K* is plotted against the normal concentration of added salt, the concentration of potassium iodide being kept constant. The results of Harned² for the alkali chlorides are plotted with dashed lines. It will be noticed that an increase in velocity is obtained with every salt but potassium sulphate, where there is a slight decrease. Walton,³

¹ Cilbrens and Francis: *J. Chem. Soc.*, 101, 2358 (1912).

² Harned: *J. Am. Chem. Soc.*, 40, 1461 (1918).

³ Walton: *Z. physik. Chem.*, 47, 185 (1904).

in the single results reported by him for a few salts, obtained a velocity change in the same direction as is here found. Further, the curves are of the same general form as those obtained by Harned for the alkali chlorides. For a given concentration of salt, his curve for sodium chloride is just below the curve for sodium bromide found here, and his curve for potassium chloride just below the potassium bromide curve found here.

Harned¹ pointed out that the salt effect on the reaction velocity was in the same order as the activity coefficients of the added salts and was of the expected order of magnitude. Recently, Harned and Åkerlöf and Harned and Douglas² have calculated the activity coefficients of all these salts by the equation

$$\log f = - \frac{u\sqrt{\sum c_i z_i^2}}{1 + A\sqrt{\sum c_i z_i^2}} + B\sum c_i z_i^{2*}$$

where f is the activity of the electrolyte divided by its mol fraction, c_i the concentration in mols per 1000 cc. of solvent, and z_i the valence of an ion of the i^{th} kind. The first number on the right is obtained from the theory of Debye and Hückel. u is a universal constant and A is a constant characteristic of each salt but which has nearly the same value for a given type of salt. The constant B is characteristic for each electrolyte and is a measure of the differences in magnitude of the activity coefficients of the electrolytes of a given type. In Table IV are given the values of B for the different salts.

TABLE VI

| Electrolyte | The Constants of the Linear Salt Effect | | | | |
|-------------|-----------------------------------------|---------------------------------|---------------------------------|---------|-------|
| | KCl | KBr | NaCl | NaBr | LiCl |
| B | 0.017 | 0.022 | 0.028 | 0.040 | 0.070 |
| Electrolyte | BaCl ₂ | SrCl ₂ | CaCl ₂ | | |
| | B | 0.0285 | 0.030 | 0.060 | |
| Electrolyte | K ₂ SO ₄ | Na ₂ SO ₄ | Li ₂ SO ₄ | | |
| | B | -0.014 | -0.005 | +0.0087 | |

The distribution of the results of velocity measurements are in a general way in the order of the B values. Had $\sum c_i z_i^2$ instead of normal salt concentration been plotted against the velocity constants, the curves of barium and strontium chlorides would fall in approximately the order of the B constants. It is interesting to note that potassium sulphate which has a negative B value decreases the velocity constant.

The univalent halides conform well, and the order of the sulphates follows that of the B values. That the situation is very complicated, however, is shown by the distribution of the curves for the alkaline earth chlorides. The

¹ Harned: J. Am. Chem. Soc., 40, 1461 (1918).

² Harned and Åkerlöf: Physik Z., 27, 411 (1926); Harned and Douglas: J. Am. Chem. Soc., 48, 3095 (1926).

*Hückel: Physik. Z., 26, 93 (1925).

B values are in the order barium, strontium and calcium chlorides, while the velocity curves are in the order strontium, calcium, and barium chlorides. When this result was obtained, all these measurements were repeated but no evidence for a re-distribution of curves resulted. Both series of results are included in Table IV and the values plotted are the mean of the two measurements for each point.

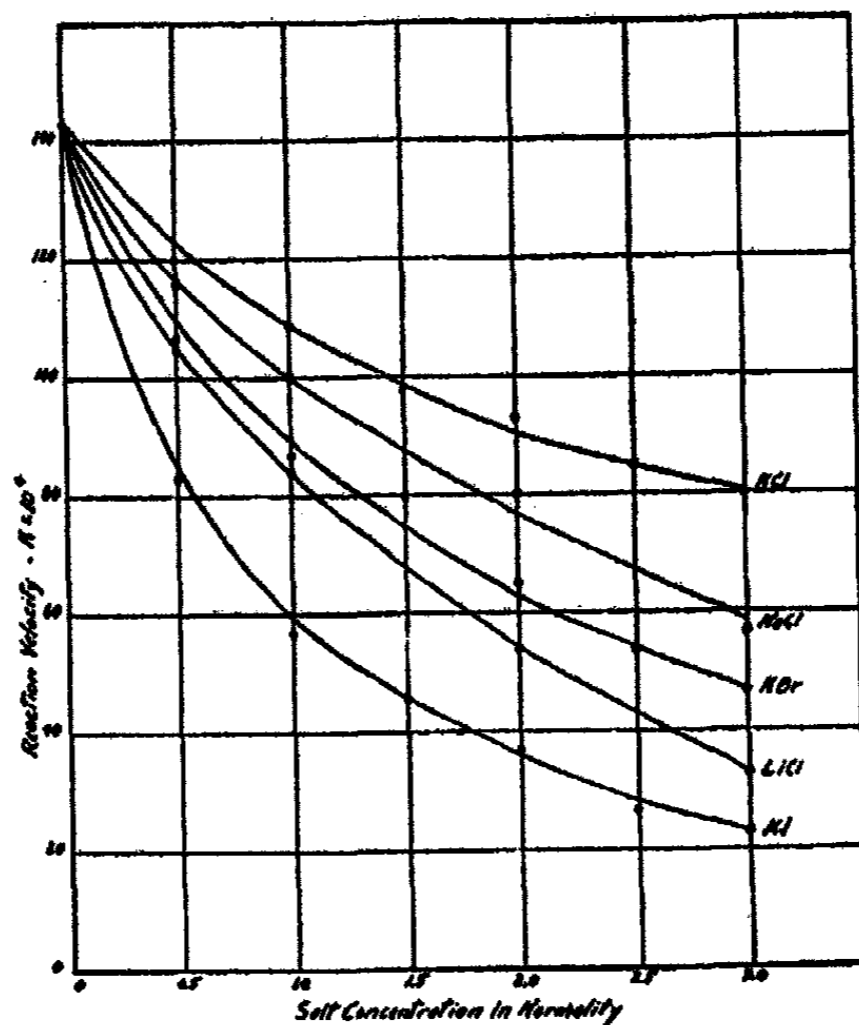


FIG. 3

Curves for the reaction velocity of the decomposition of nitrosotriacetone-amine in alkaline solutions of different salts at constant potassium hydroxide concentration of 0.014 *N* and increasing salt concentration.

The neutral salt effect is shown to be very complicated when the above results are contrasted with the hydrogen ion catalysis of ethyl acetate in neutral salt solution. In the latter case, the alkaline earth chlorides are in the order barium, strontium, calcium while the alkali halides are in the order bromide, chloride, the reverse of what is found for the iodide ion catalysis of hydrogen peroxide.

2. Nitroso-triacetone-amine Decomposition.

In Fig. 3, the reaction velocity constant of the decomposition of nitrosotriacetone-amine has been plotted against the normal concentration of salt added. In an accurate study of the decomposition of diacetone alcohol in alkali hydroxide-alkali salt solutions, Åkerlöf¹ found that the order of results was the same as the activity coefficients of the hydroxides in the salt solutions

¹ Åkerlöf: J. Am. Chem. Soc., 48, 3046 (1926).

as determined by Harned, Harned and Swindells and Harned and James.¹ This was nearly always the reverse of the neutral salt effect in hydrogen ion catalysis. Thus, the decrease in velocity constant was greatest in the order potassium chloride, potassium bromide, sodium chloride, sodium bromide, potassium iodide, sodium iodide, and lithium chloride. Although we find the order potassium, sodium, lithium chloride, and potassium chloride, bromide and iodide in agreement with the results of Åkerlöf, the general distribution of the results is considerably different.

To sum up, the distribution of the results is shown to be different in each of the four type reactions discussed. This shows conclusively that no simple explanation will suffice for all and that two factors or more are operative.

The author wishes to express his appreciation to Dr. Herbert S. Harned, at whose suggestion this investigation was carried out, and to Dr. Gösta Åkerlöf, for his helpful advice during the course of the work.

Summary

1. The velocity of decomposition of hydrogen peroxide by neutral potassium iodide and of nitroso-triacetone-amine by potassium hydroxide in a number of different salt solutions has been measured at 25°C with constant catalyst and varying salt concentrations.

2. The complicated nature of the neutral salt effect has been discussed.

¹ Harned: *J. Am. Chem. Soc.*, 47, 684, 689 (1925); Harned and Swindells: 48, 126 (1926); Harned and James: *J. Phys. Chem.*, 30, 1060 (1926).

THE CATALYTIC DECOMPOSITION OF METHANOL¹

BY DAVID F. SMITH² AND CHARLES O. HAWK³

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Introduction

In this paper are presented the results of experiments to determine the nature and effectiveness of various catalytic materials which will decompose methanol into carbon monoxide and hydrogen. The kinetic view of equilibrium in a chemical reaction shows that a catalyst which accelerates the rate of a reaction in one direction must accelerate the reverse reaction rate also. We are therefore assured that a catalyst which decomposes methanol into carbon monoxide and hydrogen will, under thermodynamically suitable conditions, form methanol from these gases. Our experiments thus have a practical interest in that they represent a very simple method for the testing of catalysts for the formation of methanol from water gas, without resorting to the use of costly and troublesome high pressure apparatus.

Approximate thermodynamic data for this reaction have already been published.⁴ These data show that at equilibrium above about 200°C., methanol vapor at one atmosphere is appreciably decomposed into CO and 2H₂; at 300° it is over 96% decomposed. High pressure, of course, favors the reaction in the direction to form methanol. At 300°C. and pressures above 100 atmospheres, practical yields of methanol may be obtained from water gas in the presence of suitable catalysts. In the absence of catalysts, however, methanol vapor remains undecomposed up to temperatures around 800°C.⁵

Although methanol has been produced from water gas on a commercial scale for some time, little information is available on the nature and action of the catalysts used. Brief statements regarding the nature of the catalysts have been made in two or three technical papers on the methanol process. In the patent literature various materials are said to be effective as catalysts. However, there is no information available on the action or relative effectiveness of these catalytic materials or on their preparation and treatment. The aim of the present work is to make available some definite information on the relative effectiveness of catalysts for this reaction and to determine the effect of promoters and method of preparation and treatment.

¹ Published by permission of the Director, U. S. Bureau of Mines (not subject to copyright). Presented before the Division of Physical and Inorganic Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., Sept. 6 to 10, 1927.

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⁴ Kelley: *Ind. Eng. Chem.*, 18, 78 (1926); Christiansen: *J. Chem. Soc.*, 128, 413 (1926); also see Smith: *Ind. Eng. Chem.* 19, 801 (1927).

⁵ Ipatiew: *Ber.*, 35, 1055 (1902).

Experimental Method

Absolute methyl alcohol from a burette at room temperature was passed through a vaporizer consisting of a coil of glass tubing immersed in boiling aniline, and then directly into a glass catalyst tube in an electric furnace. The rate of flow of the methanol was regulated by a capillary stopcock with a V-shaped notch cut in the key. The catalyst extended over but a short distance in the center of the furnace. The temperature was read by means of a thermocouple fastened to the outside of the catalyst tube. The vaporizer was fitted tightly against the furnace tube in order to prevent subsequent condensation of the methanol vapor. The undecomposed methanol was caught and weighed in a coil of tubing immersed in a mixture of carbon dioxide snow and acetone. The gaseous products passed through gas sampling apparatus and a bubbler. Since the rate of gas evolution is, over a small range, approximately independent of rate of passage of methanol over the catalyst, the rate of bubbling of gas immediately furnishes a rough measure of the activity of the catalyst. From the temperature and the known density of the methanol in the burette could be calculated the weight of methanol used. This weight was compared with the weight of methanol caught in the condenser and the fraction decomposed thus determined. The composition of the gaseous decomposition products was determined in most of the experiments.

The catalyst in all cases extended over a length of 8.5 cm. in a glass tube 1.6 cm. in internal diameter. The gross volume of catalyst was thus 17.1 cc. The tube was supported horizontally, the catalyst being held in position by plugs of glass wool. In the earlier experiments the catalyst in the form of a dried cake was broken into uniform pieces just small enough to pass through a glass tube 0.7 cm. in internal diameter. In later experiments the catalyst in the form of a moist paste was passed through a press which produced a cylindrical thread of about 2.8 mm. diameter. This thread, after drying, was cut into pieces about 7 mm. in length. In the latter way catalysts were obtained of fairly uniform surface and porosity. Different preparations of the same catalyst by a uniform method checked fairly well in activity. All catalysts were dried in air at 80° to 100°C. immediately after they were run through the press and were usually subjected to a preliminary reduction at 300°C. by hydrogen before placing them in the catalyst tube, since appreciable shrinkage in volume sometimes occurred in the process.

Preparation of Catalysts

1. Pure commercial chromic anhydride (CrO_3) with a small amount of water was added to high grade commercial zinc oxide. The atomic proportions of Zn:Cr varied from 10:1 to 1:1 as indicated below. The resulting paste, which was ground thoroughly together in a mortar, was pressed into appropriate form for use, dried at 100° and reduced with hydrogen or methyl alcohol vapor at 300°.

2. A solution of sodium chromate was added to a solution of pure zinc nitrate. The precipitate was washed free of nitrate, dried and reduced as above.

3. A solution of sodium carbonate was added to a hot solution of zinc nitrate. The precipitate was washed, dried, placed in a tube heated to 350° , and evacuated until no more carbon dioxide was evolved.

4. A solution of ammonium hydroxide was added to a solution containing zinc and chromium nitrates in the ratio 4 Zn to 1 Cr. The precipitate was washed, dried at 80° in air and then in a current of hydrogen at 300° .

5. Normal zinc chromate was made according to Gröger.¹ The saturated solution of chromic acid was shaken for several days with the proper amount of zinc oxide. The solid was ground up several times during the shaking. The chromate was then filtered free of the supernatant liquid and treated as above.

6. Zinc chromite was precipitated by mixing solutions of zinc nitrate and of chromium chloride dissolved in an excess of sodium hydroxide. The precipitate was washed and dried as above.

7. Copper hydroxide equal to 5% of the weight of the zinc oxide was added to the preparation (1) before addition of the chromic acid. Zn:Cr = 4:1.

8. Dry zinc carbonate (prep. 3) was mixed with moist, precipitated chromium hydroxide in the atomic proportions Zn:Cr = 4:1. The product was washed, dried and heated to 350° in a vacuum as above.

9. A solution of sodium carbonate was added to a solution of zinc and chromium nitrates in the ratio 4 Zn:1Cr. The precipitate was washed and dried as before, and then heated to 350° in a current of methanol for 45 minutes.

10. Cadmium chromate was prepared as for zinc chromate in prep. (2).

11. Cadmium chromate was prepared as for zinc chromate in prep. (1), the proportions being 1Cd:1Cr. This preparation was reduced with hydrogen at 200° .

12. Cadmium carbonate, prepared by adding a solution of sodium carbonate to a hot solution of cadmium nitrate and washing, was heated in a vacuum for 15 minutes at 400° . The surface of the product was brown, due to formation of the oxide, while the interior was light yellow.

13. A hot solution of cadmium and manganese chlorides, in the proportions of 4Cd:1Mn, was precipitated with a solution of potassium hydroxide. The precipitate was washed and dried in air at 100° and then in hydrogen at 300° .

14. A solution of uranyl nitrate was boiled with cadmium hydroxide. The proportions were 1Cd:1U. The product was dried and reduced as usual.

15. 39 g. moist cadmium hydroxide was mixed with 48 g. moist zinc hydroxide. The product was dried in air at 80° and then in hydrogen at 350° .

16. Zinc uranate was prepared by boiling zinc carbonate with a solution of uranyl nitrate until no more CO_2 was evolved. The proportions were 1Zn:1U. The product was dried and reduced as usual.

¹ Z. anorg. Chem., 70, 135 (1911).

17. An excess of a solution of zinc nitrate was added to a solution of ammonium vanadate. Ammonia was added to the mixture slowly with stirring until most of the vanadium was precipitated. The precipitate was washed, dried and reduced with hydrogen at 300° , and later with methanol.

18. Vanadic acid was made by boiling a concentrated solution of ammonium vanadate with nitric acid. The precipitate was washed and boiled with zinc hydroxide. The product was reduced with hydrogen and methyl alcohol at 300° - 350° . The proportions were (a) $4\text{Zn}:\text{V}$ and (b) $10\text{Zn}:\text{V}$.

19. Zinc molybdate was made by mixing solutions of zinc nitrate and sodium molybdate. The product was washed, dried and reduced with hydrogen at 300° .

20. A hot solution of zinc and aluminum sulfates was precipitated by adding ammonia. The proportions were $4\text{Zn}:\text{Al}$. The precipitate was washed free of sulfate, dried at 100° and then at 300° in a current of hydrogen.

21. A hot solution of zinc nitrate and ferric chloride was precipitated with ammonia. The proportions were $4\text{Zn}:\text{Fe}$. The precipitate was washed, dried, and reduced at 300° .

22. A hot solution of zinc nitrate and manganous chloride was precipitated first with ammonia and then with potassium hydroxide. The proportions were $4\text{Zn}:\text{Mn}$. The precipitate was washed, dried, and reduced with hydrogen at 300° .

23. 60 g. of moist ammonium uranate and 9 g. moist copper hydroxide were mixed and dried at 85° . The mass was then heated in hydrogen at 400° - 500° .

24. 14 g. of the moistened preparation (23) were mixed with 3.6 g. moist zinc oxide. The product was reduced in hydrogen at 400° for 5 hrs.

25. A high grade commercial zinc oxide (made by burning pure zinc) was moistened with water, pressed and dried.

26. A solution of zinc nitrate was precipitated with ammonia. The precipitate was washed, pressed and dried.

27. Acid-washed pumice was saturated with a solution of zinc nitrate. The mass was heated for several hours at 300° in a current of hydrogen.

28. Ammonia was added to a hot solution of zinc and beryllium nitrates in the proportions $4\text{Zn}:\text{Be}$. The precipitate was washed and dried as usual.

29. Ammonia was added to a hot solution of beryllium nitrate. The precipitate was washed and dried as usual.

30. The beryllium oxide from prep. (29) was mixed with chromic acid in the proportions $4\text{Be}:\text{Cr}$. The product was dried in air at 80° and then in hydrogen at 300° .

31. Magnesium oxide was mixed with chromic acid in the proportions $1\text{Mg}:\text{Cr}$. The product was dried in air at 80° and then in hydrogen at 300° .

32. A mixture of magnesium and ferric hydroxides was prepared in the proportions $4\text{Mg}:\text{Fe}$ as for prep. (21).

33. Magnesium uranate was made from magnesium oxide as for zinc uranate in prep. (16).

34. A solution of sodium chromate was added to a warm solution of strontium nitrate. The precipitate was washed by decantation several times. It was dried, pressed and reduced with hydrogen at 300°.

35. A hot solution of chromium nitrate was precipitated by ammonia. The precipitate was washed, dried in air at 80° and then in hydrogen at 300°.

36. The vanadic acid as in prep. (18) was dried, pressed and reduced, first with hydrogen at 300° and then with methanol at 300° and at 350°.

Experimental Results

The experimental data are presented in Figs. 1 and 2 and in Table I. Fig. 1 shows the type of curves obtained at different rates of flow of methanol

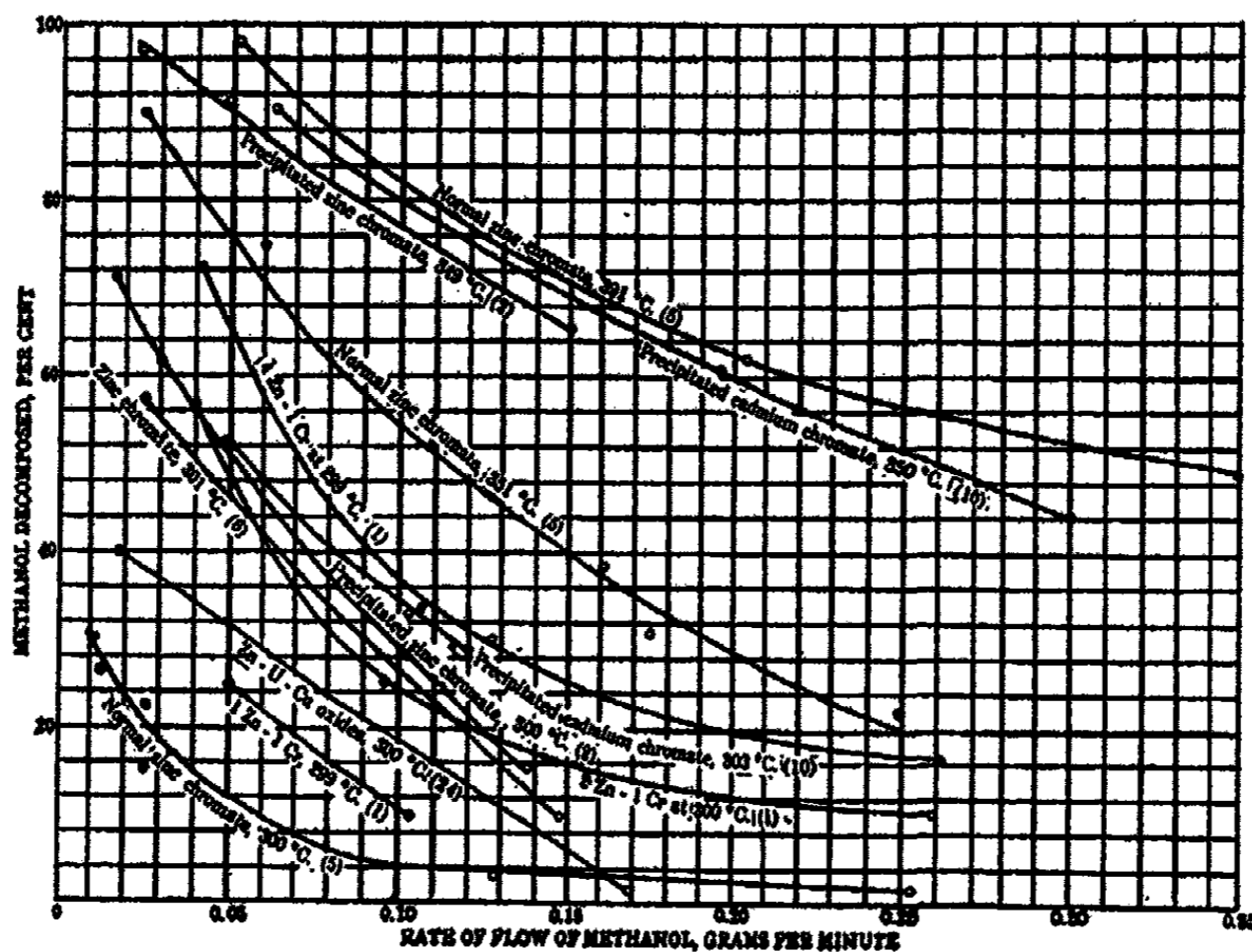


FIG. 1
Efficiency of Catalysts

over the catalyst and at different temperatures. Table I contains the data which are not included in Figs. 1 and 2. In Table I and Fig. 2 the rate of flow of methanol is in all cases 0.08 g. per minute. This rate of flow over the 17.1 cc. of catalyst at 300° represents a space velocity of 412 in the usual units of volumes of gas per hour per unit volume of catalyst. In all experiments referred to hereinafter, except as noted otherwise, the rate of flow was 0.08 g./min., the temperature of the catalyst during the test was 300°, and the volume of catalyst was 17.1 cc. All of the catalysts for which the data are presented in Fig. 1 were merely broken into uniform pieces and not run through the press. This is also the case for the lower curve of Fig. 2. The numbers in parentheses on the curves of Fig. 1 indicate the preparation numbers for the respective catalysts.

The data in Fig. 1 indicate that the normal zinc chromate, prepared as in method (5) by long continued mixing of ZnO with an excess of chromic acid, is less active than the catalyst containing the same proportions of zinc and chromium but made as in method (1) by merely adding to ZnO the requisite amount of chromic acid in a small amount of water. This is probably due to the fact that in the former case, more opportunity is given for the chromate crystals to grow. The activity of the catalyst made as in method (1) and containing 2Zn:1Cr is however about the same as the activity of the precipitated catalyst containing the same proportions of zinc and chromium. Cadmium chromate, although it reduces in use, still retains a considerable ac-

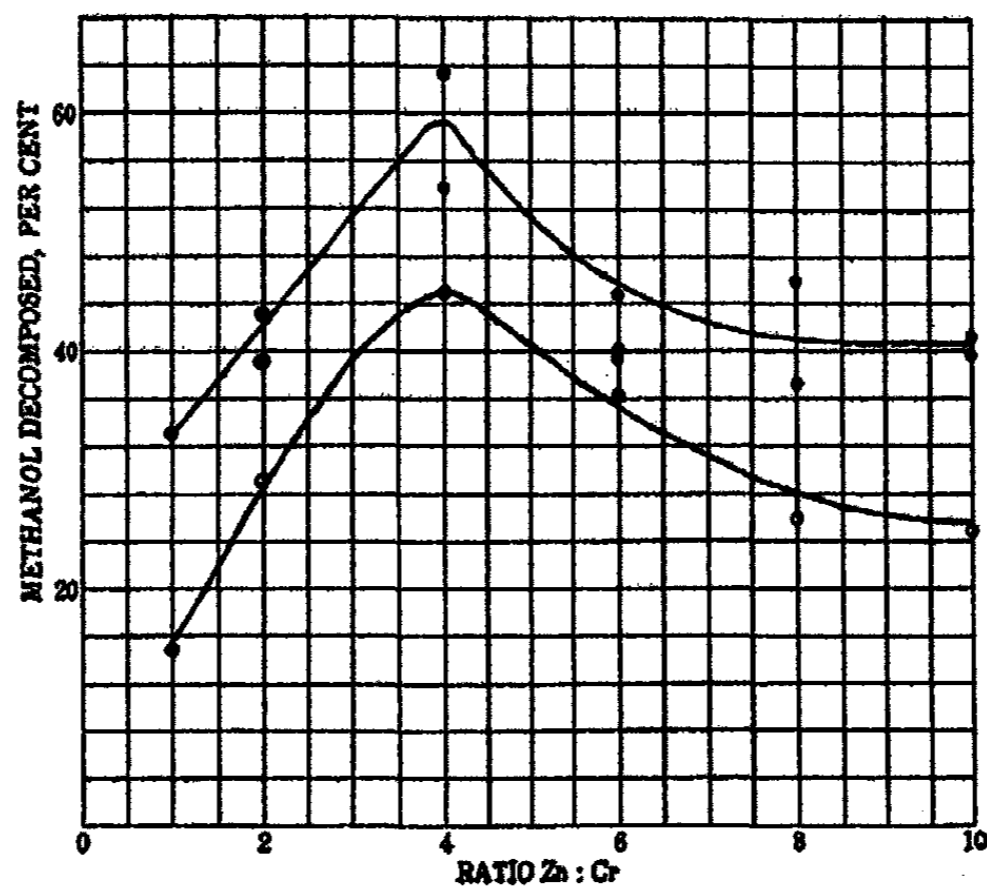


FIG. 2
Effect of composition on catalytic activity

tivity—probably somewhat greater than that of the corresponding zinc chromate. The curves also show that the activity of the zinc-chromium catalysts increases as the ratio of zinc to chromium increases from 1 to 4.

Fig. 2 shows that there is an optimum ratio of zinc to chromium at about the atomic proportions 4Zn to 1Cr. All of the catalysts used here were made by a uniform procedure (No. 1). The two curves represent the data on two series of preparations having somewhat different surface areas as explained previously. They both show a maximum of activity in approximately the same place. The points for the upper curve also show the order of reproducibility obtainable, each point representing a separate preparation of the catalyst.

In Table I the best catalysts have, in general, been placed first. ZnO from the carbonate and the 4Zn:1Cr catalyst (method 1) are of about equal activity. The zinc-chromium catalyst made by precipitating the hydroxides with ammonia appears to be somewhat less active than that made from ZnO

TABLE I. ADDITIONAL DATA ON CATALYSTS

Rate of Flow of Methanol, 0.08 g./min. Gross Volume of Catalysts, 17.1 cc.

| Catalyst | Prep. No. | Temp. | Decomp. per cent | CO | Gas analysis | | CH ₄ , etc. |
|--------------------------------------|-----------|-------|---------------------|----|----------------|-----------------|------------------------|
| | | | | | H ₂ | CO ₂ | |
| 4 Zn:1 Cr | 1 | 300 | 58.6 | 29 | 68 | 2 | 0.5 |
| ZnO | 3 | 300 | 61.7 | 30 | 67 | 1 | 0.8 |
| 4Zn:1 Cr | 4 | 300 | 54.8 | 27 | 68 | 4 | 0.9 |
| 4Zn:1 Cr | 8 | 300 | 62.4 | | | | |
| 4Zn:1 Cr | 9 | 300 | 60.8 | | | | |
| 1Zn:1U | 16 | 300 | 43.2 | 23 | ? | 5 | ? |
| Zn-V | 17 | 300 | 83.5 | 11 | 56 | 16 | 15 |
| 4Zn:1 V | 18a | 300 | 64.6 | 11 | 56 | 16 | 16 |
| 10Zn:1 V | 18b | 300 | 61.3 | 10 | ? | 14 | ? |
| 10Zn:1 V | 18b | 300 | 28.6 | 15 | ? | 9 | ? |
| ZnO* | 27 | 305 | 2.6 | | | | |
| ZnO | 25 | 300 | 13.0 | 25 | 71 | 2 | 0.8 |
| Zn-Cr* | 6 | 302 | 18.7 | 7 | 74 | 16 | 2.6 |
| ZnO-MnO | 22 | 300 | 2.6 | | | | |
| ZnO-Fe ₂ O ₃ | 21 | 300 | 1.5 | | | | |
| ZnO-Fe ₂ O ₃ | 21 | 350 | 23.5 | 12 | 45 | 13 | 14 |
| ZnO-Al ₂ O ₃ | 20 | 300 | 3.0 | | | | |
| ZnO-BeO | 28 | 300 | <1.0 | | | | |
| Zn-Mo | 19 | 300 | 3 | | | | |
| Zn-Mo | 19 | 348 | 21 | 11 | 56 | 17 | 14 |
| Zn-Mo | 19 | 399 | 81.5 | | | | |
| CdO | 12 | 300 | 11 | 4 | 64 | 31 | 0.4 |
| CdO-Cr ₂ O ₃ | 11 | 203 | 9.4 | 22 | 73 | 4 | 0.6 |
| CdO-MnO | 13 | 300 | 4.1 | | | | |
| CdO-U | 14 | 300 | 8.7 | | | | |
| CdO-ZnO | 15 | 350 | 14.9 | | | | |
| MgO-Cr ₂ O ₃ | 31 | 299 | 5.0 | | | | |
| MgO-Cr ₂ O ₃ | 31 | 348 | 30.0 | 18 | 73 | 8.0 | 1.4 |
| MgO-Fe ₂ O ₃ | 32 | 301 | 2.0 | | | | |
| MgO-Fe ₂ O ₃ | 32 | 350 | 9.5 | | | | |
| MgO-U | 33 | 297 | 7.6 | | | | |
| BeO | 29 | 302 | 2.1 | | | | |
| BeO-Cr ₂ O ₃ * | 30 | 302 | 28.1 | | | | |
| SrO-Cr ₂ O ₃ | 34 | 302 | 0.0 | | | | |
| Cr ₂ O ₃ | 35 | 302 | 53.8 | 7 | ? | 17 | ? |
| V ₂ O ₅ | 36 | 303 | 32.1 | 16 | 14 | 11 | 57 |
| Cu-*UO ₂ | 23 | 324 | 4.5 | 4 | 87 | 0.3 | 5 |

*The catalyst in these experiments was broken into pieces instead of run through the press, as described above. The relative surface by the two methods can be obtained from Fig. 2.

and chromic acid. The former also gives somewhat more CO_2 in the gases of decomposition. ZnO from the carbonate is not further activated by mixture with chromium hydroxide. Reference from Table I to Fig. 2 shows that the Zn-U catalyst is more active than the Zn-Cr catalyst of the same atomic proportions. It gives about the same amount of CO_2 in the gas as does the Zn-Cr catalyst made from the hydroxides. Zinc-vanadium catalysts give very large decompositions but much of the carbon appears as CO_2 . Beryllium chromate, placed near the bottom of the Table, is also a fairly good catalyst.

Cadmium chromate, since it gives a considerable decomposition even at 203° , seems more active than zinc chromate—at least before it has suffered appreciable reduction. Magnesium chromate, however, is less active than zinc chromate. It seems likely, then, that the least stable chromate of these is the most active catalyst.

The zinc chromite which was precipitated from strongly alkaline solution had about the same activity as that of ordinary precipitated zinc chromate.

Although it is reported by Audibert¹ that the so-called sub-oxides of chromium and uranium are good catalysts, it is evident from Table I that these oxides as they were prepared in the present work are not good catalysts. It is rather the mixtures of these oxides with zinc oxide which are good catalysts. Uranium oxide alone seems to produce chiefly a decomposition to formaldehyde and hydrogen, as the gas analysis and tests on the condensate showed. Chromium oxide gave a large decomposition but much of the carbon appeared as CO_2 . Furthermore, about 50% of the condensate in the latter case evaporated while the condenser was warming from the temperature of carbon dioxide snow to room temperature. The nature of this volatile product was not determined, but it is probably methyl ether. It is evident, however, that the catalytic effect of these oxides alone is specific and quite different from that of their mixtures with zinc oxide. Very little of the specific catalytic effect of the chromium or uranium oxides appears when these oxides are mixed with ZnO . Some light was thrown on this point through preliminary results of X-ray powder photographs of these substances which were taken with the assistance of Mr. F. E. Frey. X-ray photographs of ZnO and of Cr_2O_3 showed, of course, the characteristic lines of these substances. A simple mixture of these two dry oxides in the atomic proportions of 2Zn to 1Cr showed the lines of both oxides. The precipitated zinc chromate showed its characteristic lines. After the latter had been reduced at 300° with hydrogen and used as a catalyst it assumed a grayish appearance and presumably was a mixture of ZnO and Cr_2O_3 . Its powder photograph, however, showed none of the lines of Cr_2O_3 and only the apparently undisplaced lines of ZnO together with three faint extraneous lines and a slight general blackening of the film. The atomic proportions of zinc to chromium in this chromate should be 2:1. A catalyst with the same proportions of zinc and chromium made by method (1) was also photographed after it had been reduced. It showed the same thing as did the reduced precipitated chromate. It is likely, then that the

¹ *Chimie et Industrie*, 13, 186 (1925).

Cr_2O_3 in these catalysts does not exist in the ordinary form. It is perhaps either amorphous or has combined with ZnO . This would, then, explain why in the mixed catalyst the specific catalytic effect of the Cr_2O_3 does not appear. It is perhaps worthy of remarking in this connection that ZnO and Cr_2O_3 both have hexagonal crystal structure and there is the possibility of solid solution or mixed crystal formation. BeO , also hexagonal, makes a fairly good catalyst in the presence of Cr_2O_3 .

One experiment was made on a zinc chromate catalyst (method 5) in which nitrogen saturated with methanol at room temperature (v.p. roomm.) was passed over the catalyst. The same per cent decomposition was effected as with methanol at atmospheric pressure. The rate of the decomposition reaction thus is first order with respect to the pressure of methanol.

A number of experiments were made on ZnO alone. A product made by precipitation of hot zinc nitrate solution with ammonia (method 26) gave, at 300° and the usual rate of flow of methanol, about 3-4% decomposition. A commercial ZnO , made by burning zinc vapor, gave 13%. It was found, however, that subsequent treatment greatly altered the activity of the ZnO . For example, this same catalyst of commercial ZnO , after use in an experiment at 300° , was cooled to room temperature in an atmosphere of dry CO_2 , then reheated to 300° in an atmosphere of methanol. It now gave 27.5% decomposition. The process was repeated, except that the catalyst was inadvertently heated to 400° just before testing. It now gave 35.4% of decomposition. This catalyst after standing at room temperature in a stoppered bottle for several weeks gave on retesting 16% decomposition. Another sample of the same commercial ZnO at first gave 9.7% and then after heating to 400° for $\frac{1}{2}$ hour and again testing at 300° gave 22% decomposition. After this test the catalyst was heated to 350° in an atmosphere of methanol and again tested at 300° . It still gave 22%. This process was repeated with a fresh sample of ZnO . It first gave 13.0% and after heating to 400° for 15 minutes gave 25.1%. After heating to 400° for 1 hour in an atmosphere of methanol this catalyst had decreased in activity to 6%. The catalyst was then allowed to cool in a stream of CO_2 and was kept overnight in an atmosphere of CO_2 . The next morning the catalyst was heated to 350° for 45 min. in a stream of methanol. It then gave 15.5% decomposition at 300° . The ZnO catalyst is thus affected both by heat treatment and by the presence of dry CO_2 . It was found that the ZnO made from precipitated hydroxide could also be affected in the same way.

An experiment was made with a zinc chromate catalyst to which had been added about 5% of copper hydroxide (prep. 7). The reduction of the chromate was carried out at 250° instead of 300° and a test was made at 300° . A somewhat larger decomposition was obtained than with this catalyst without copper but this result was found to be due to incomplete reduction. A subsequent test gave the usual decomposition.

A zinc-chromium catalyst (at proportions 4:1) which had been standing in a stoppered bottle for several weeks was again tested. It gave 67.3% instead of the usual 59%. After passing a stream of CO_2 over this catalyst the temperature was let fall from 300° to room temperature and the catalyst

was left overnight in an atmosphere of CO_2 . It was then tested and gave 83% decomposition. The passage of moist CO_2 over this catalyst brought the decomposition down to 48%.

The materials used in the preparation of the catalysts were not specially purified: Commercial c.p. chemicals were used. Tests, however, showed the absence of iron and of manganese. The small amounts of CO_2 and CH_4 formed in the experiments can hardly be due to the presence of impurities in the materials used and must be considered as by-products whose formation is catalyzed by the same materials which catalyze the principal reaction. In the case of the Zn-Cr catalysts the amounts of CO_2 and CH_4 did not vary much with changing proportions of zinc and chromium.

The catalysts containing uranium and vanadium were hard to reduce and were pyrophoric. The chromium catalysts, however, did not seem to oxidize when brought into the air after use.

Some of the earlier experiments recorded here were made with the assistance of Mr. Cyrus G. Dunkle to whom the authors wish to express their thanks.

The authors wish to take this opportunity to express their appreciation to Mr. A. C. Fieldner whose interest and encouragement as Chief Chemist of the Bureau of Mines made this work possible.

Summary

1. The decomposition of methanol vapor on various catalytic materials has been measured. Zinc oxide made by igniting zinc carbonate; mixtures of zinc oxide and chromic acid in the atomic proportions $4\text{Zn}:\text{Cr}$; mixtures of zinc oxide and uranium oxide and, perhaps, also mixtures of zinc oxide and vanadium oxide and of cadmium oxide and chromic acid would be considered very good catalysts for the decomposition of methanol into carbon monoxide and hydrogen. These substances should also be good catalysts for the formation of methanol from water gas.

2. The activity of pure ZnO and also of zinc oxide-chromium oxide catalysts is to a considerable degree dependent on the heat and other treatment to which they are subjected.

3. The specific catalytic effect of pure chromium oxide is absent in the zinc oxide-chromium oxide catalysts. X-ray powder photographs indicated the reason for this.

4. Practically all catalysts studied yielded at least a small amount of CO_2 in the gases of decomposition. The CO_2 probably is not due to foreign material in the catalyst but is to be regarded as a by-product of the principal reaction.

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August 30, 1927.*

TEMPERATURE OF COAGULATION OF PURE COPPER COLLOIDAL SOLUTION

BY B. M. REID AND E. F. BURTON

I. Introduction

The original intention of the experiments detailed herewith was to determine the relation between temperature and coagulation in Bredig copper sols to which electrolytes had been added. As the work developed it was shown that there are indications that for every given sample of such col-

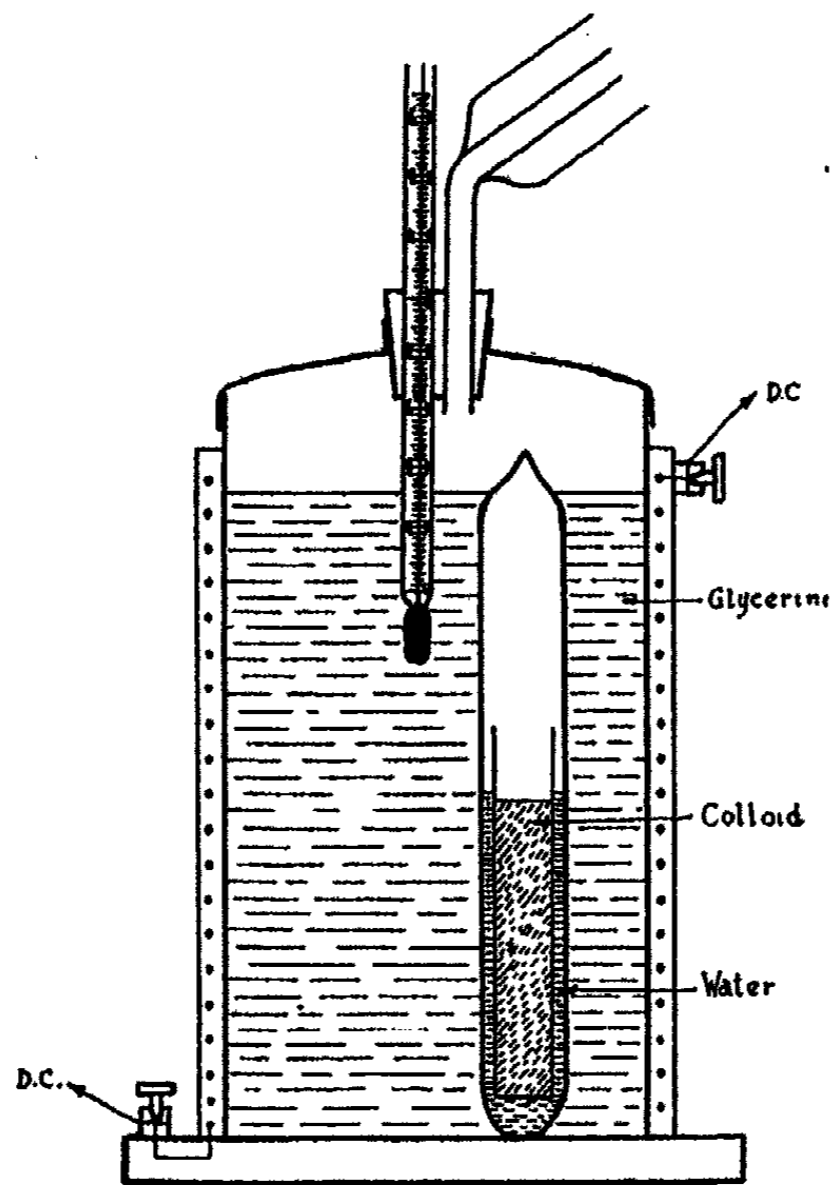


FIG. 1

loidal solution even when practically free from electrolytic impurities there exists a definite temperature at which coagulation takes place automatically.

The references in the literature to temperature effects have chiefly to do with the change in the velocity of electrolytic coagulation with temperature. Regarding the influence of merely heating pure colloidal solutions, Freundlich¹ says: "Sols behave very differently upon simple warming, even

¹ Freundlich: "Colloid and Capillary Chemistry", p. 467.

without the addition of a coagulant. Many such, as numerous sulphides, (e.g. arsenious and gold), hydroxides (e.g. ferric), metals (e.g. gold sols in alkaline solution) bear long continued boiling without flocculating; others, as in particular many metallic sols, (e.g. platinum) coagulate quickly on warming." Most of these references are to work before 1900, when the influence of small traces of impurity dissolved from the glass vessels may have been lost sight of; at any rate, conditions were complicated by allowing ebullition to take place thus causing constant violent stirring of the sol.

2. Experimental

a. *Method:* The procedure in the following experiments was very simple; a sample of colloid was sealed in a tube which was heated to any desired constant temperature for half an hour. No ebullition took place at any time. Fig. 1 shows the arrangement of the apparatus. The tube containing the colloid was enclosed in a sealed Pyrex tube which was heated in a glycerine bath.

The arrangement for heating the glycerine is shown in the diagram. The electric furnace consisted of a cylindrical copper vessel 19 cms. in height and 11 cms. in diameter, surrounded by a coil of wire which was covered with asbestos to within 1 cm. of the top. A copper lid fitted tightly over the top of the furnace which was filled with glycerine having a boiling point of 290°C. The end of the condenser for the glycerine and a thermometer of range 0°C to 200°C were inserted in a cork fitting into an opening in the centre of the lid. The furnace was connected to the 110 D.C. in series with a Zenith variable resistance coil and an ammeter.

The first determinations were attempted using ordinary glass tubes and afterwards Pyrex tubes as containers of the colloid sample. It was found, however, that as the temperature was raised impurities dissolved from the glass, and produced coagulation. This was detected by the very great increase in the conductivity of the sol after heating. With the substitution of a copper tube as the inner container, this difficulty was eliminated; the resistance was always measured both before and after every determination, as a check on the introduction of impurities. There was almost invariably some decrease in resistance, but, where this decrease was great enough to be comparable to the addition of an active electrolyte, the result was discarded.

The copper tube used was cylindrical in shape, 10 cms. long and 1.5 cms. in diameter; the most convenient amount of colloid to use in a tube of this size was found to be 12 cc. After this amount of solution was placed in the tube the resistance was measured, using two platinum electrodes made so that they could be inserted directly into the copper tube. When not in use, these electrodes were kept in conductivity water to insure cleanliness. The tube containing colloid was then dropped onto glass wool in the bottom of a thick-walled Pyrex tube, of diameter about 2 cms. Water was introduced into the glass tube up to about 2 cms. from the top of the copper tube by means of a long narrow funnel and the tube was then sealed off at a length of about 17 cms.

TABLE I

| Date of Experiment | Temperature maintained °C | Final observation |
|--------------------|---------------------------|---------------------|
| Feb. 26 | 196 | coagulation |
| Mar. 4 | 160 | no coagulation |
| " 5 | 175 | " " |
| " 6 | 180 | " " |
| " 8 | 185 | " " |
| " 9 | 190 | " " |
| Mar. 29 | 170 | coagulation |
| " 30 | 160 | " |
| Apl. 1 | 150 | no coagulation |
| Apl. 22 | 150 | partial coagulation |
| " 23 | 155 | coagulation |
| " 24 | 145 | no coagulation |

Half an hour to one hour was taken to raise the temperature of the glycerine to the desired point using a current of about 5 amps., which was then reduced to a value that would maintain the given temperature for one half hour. At the end of this time the tube was removed and allowed to stand at room temperature for four hours. Then the glass tube was opened, the copper tube removed, and the resistance again measured, thus checking the introduction

TABLE II

| Date of experiment | Temperature maintained °C | Final observation |
|--------------------|---------------------------|-------------------|
| Oct. 21 | 140 | no coagulation |
| " 22 | 150 | " " |
| " 25 | 160 | " " |
| Nov. 3 | 170 | " " |
| " 4 | 180 | coagulation |
| Nov. 10 | 175 | coagulation |
| " 11 | 170 | " |
| " 13 | 165 | " |
| " 15 | 160 | no coagulation |
| Dec. 8 | 140 | coagulation |
| " 9 | 100 | no coagulation |
| Dec. 16 | 115 | coagulation |
| " 18 | 109 | no coagulation |

Jan. 4, 1927, colloid in stock bottle coagulated.

of coagulating factors other than the temperature. The colloid was then poured into a test-tube and it was observed whether it had coagulated or not.

b. *Results.* (i) The first solution of copper colloid with which experiments were carried out was made by sparking wires in 2400 ccs. of conductivity water. *After the colloid was made 24 drops of 0.1N potassium chloride were added.* The results obtained are given in Table I, which shows the temperature at which coagulation takes place as the colloid sample ages.

After an absence of four months the colloid was found coagulated on September 15.

(ii) The second solution tested was copper colloid made by sparking wires in 2400 ccs. conductivity water *to which had been added just before sparking 20 drops of 0.1 N potassium hydroxide solution.* This colloid was made on October 7, 1926, and Table II gives the results.

The date of each determination is given and the results are divided into groups on this basis. In each group temperatures have been obtained showing the limits of coagulation and no coagulation; the mean of these temperatures might be called the temperature of coagulation of the colloid at that particular time in its history.

The two samples for which the above results were obtained were evidently undergoing slow coagulation, in which process the size of the particles increases until it exceeds the limiting size for which the Brownian movement masks the gravitational pull and the particles settle out of the suspension. It is apparent, then, that this temperature of coagulation decreases as the particles increase in size.

(iii) For a suspension of copper in conductivity water such that an equilibrium state exists when the coagulation is extremely slow, the temperature of coagulation would be a unique property of the solution and a function of the size of the particles. It was thought that it might be possible to determine the form of this function and for this purpose a third sample of copper colloid was prepared by the same method of sparking between wires. This time the sparking was done in conductivity water *to which no electrolyte was added either before or after the sol was made.* Then three samples of 200 ccs. each were transferred to carefully cleaned bottles, which had been allowed to soak in successive washes of conductivity water for two weeks. Six, fifteen, and twenty-four drops of 0.01 N potassium chloride solution were added to these three samples respectively, and they were allowed to stand undisturbed for a week or ten days before any determinations were made. Table III gives for each solution the limits of temperature between which lies the coagulation temperature of the solution.

Whether the solutions in which the electrolyte was added were undergoing slow coagulation or had attained a condition of equilibrium is doubtful. It seems, however, certain that in the case of the stock solution a condition of equilibrium exists. At any rate there appears to be a definite relation between the coagulation temperature and the concentration of electrolyte, and a curve, Fig. 2, has been drawn for the values obtained. For the three solutions containing electrolyte the relation is very nearly linear. Under the conditions

TABLE III

| Concentration of electrolyte - KCl - | Uncoagulated at Temperature | Coagulated at Temperature | Days after addition of electrolyte |
|--------------------------------------|-----------------------------|---------------------------|------------------------------------|
| 0 | 180°C | 185°C | |
| 0.97×10^{-6} | 142°C | 146°C | 33 |
| 2.40×10^{-6} | 138°C | 140°C | 20 |
| 3.84×10^{-6} | 131°C | 134°C | 19 |

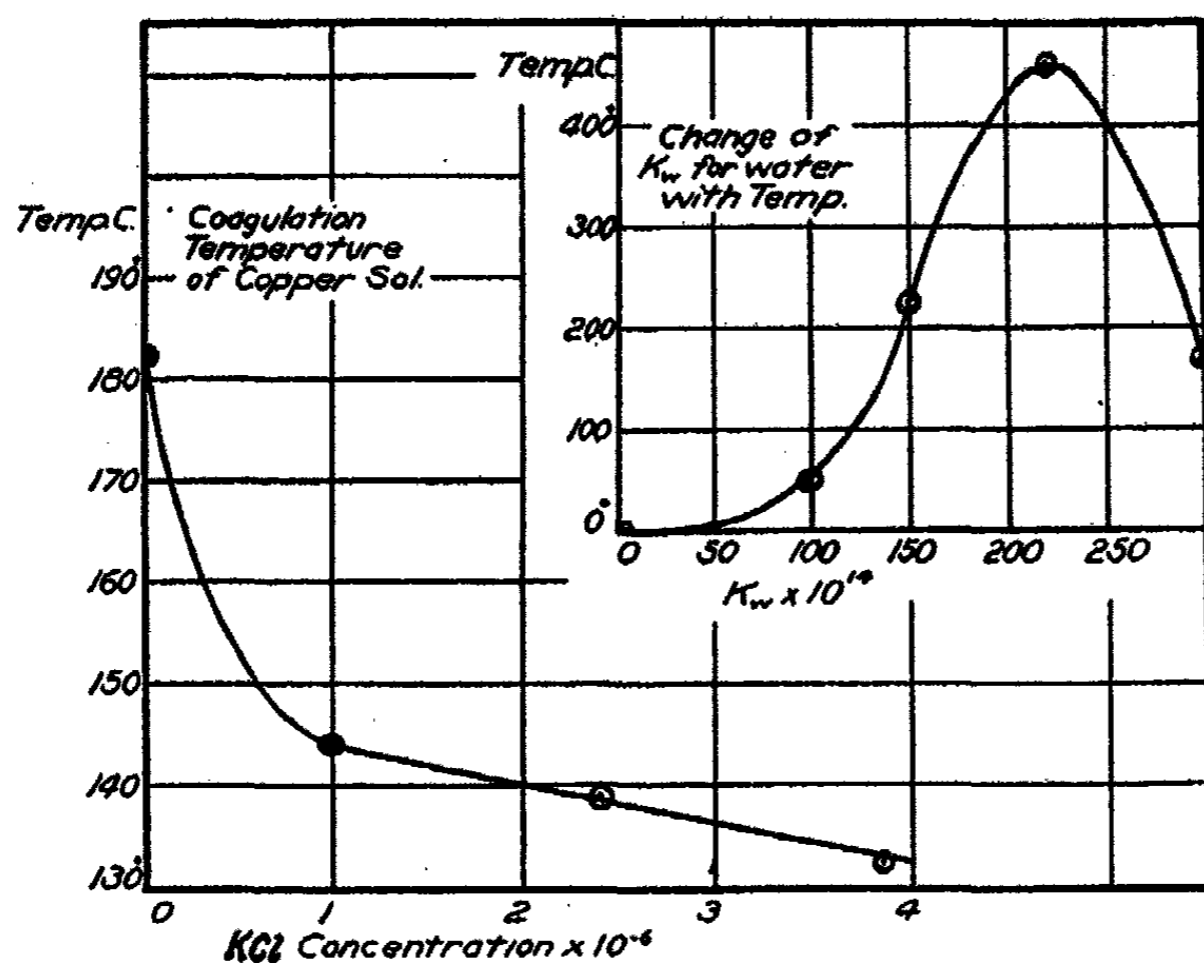


FIG. 2

of the experiment for these results to be strictly comparable, if the solutions were slowly coagulating, determinations should have been made when the same time had elapsed after the addition of electrolyte for each solution. If this had been done and the determination of the coagulation temperature for the solution with a concentration of KCl 0.97×10^{-6} had been made 20 days after the addition of electrolyte the result would have been slightly higher and the curve for these three points more exactly a straight line. The assumption that the temperature of coagulation would have been higher at that time is justified from the results given previously.

It is consistent with colloidal theory in connection with coagulation to assume that the solutions to which increasing amounts of electrolyte were added will contain particles of correspondingly increasing sizes at least after the same interval of time has elapsed since the electrolyte was added.

Hence the results agree in indicating that the coagulation temperature is a function of the size of the particles.

Attempts were made to observe the difference in size of the particles by means of the ultramicroscope count. These did not yield definite results, but exact measurement of the light scattered by the various samples showed a progressive change as the amount of electrolyte added increased.

3. Theoretical Considerations

We undoubtedly have to do with two separate cases:

(i) The purest and simplest form of sol can be coagulated by increase of temperature alone, and

(ii) During the process of slow coagulation induced by traces of electrolyte, coagulation may be made "rapid" by increase of temperature.

These experimental results confirm a very simple view of what is going on in such a colloidal solution as this copper sol. There is not the slightest doubt that such sols as these Bredig metal sols exist practically unchanged for great lengths of time without the aid of protective colloids; of course, one may say that there is always slow coagulation, which is a relative term, but the rate of coagulation for many of these sols is at the best very very slow. This stability is due to (1) the slow rate of fall of small particles under gravity, (2) the disturbance due to the Brownian movement, and (3) the prevention of any noticeable coalescence of particles due to their mutual repulsion.

In presenting the theories of rapid and slow coagulation, Smoluchowski¹ arrived at formulae which indicate the way in which the number of particles of various sizes in a suspension will vary with time due to the aggregation as a result of collisions brought about by the Brownian movement. The assumption is made, following Zsigmondy, that around each particle is a sphere of attraction of definite radius, and, if two particles approach during molecular motion so closely that the centre of one enters the sphere of attraction of the other, they would remain adherent and not separate again. But this assumption is not necessary to the establishment of the Smoluchowski formulae; in fact, the experimental confirmations of these formulae show that the two particles reach this critical position when they touch or nearly so. If they touch, surface tension forces would account for their sticking together.

The simplest explanation seems to be that, as a result of the molecular motion in the liquid medium, the particles are driven hither and thither, and collisions certainly would be very frequent if there were no forces tending to keep the particles separated. Frequent collisions are prevented by the natural repulsion of the particles due to their like electrical charges. The mutual repulsion is not exercised until two particles are quite close together but the force can be very great when the particles approach one another very closely. The reason lies in the distribution of the Helmholtz layer; it is quite generally accepted now that this outer layer is diffuse, as suggested by Gouy,² and that it may be several molecular diameters in thickness. When two neighboring particles approach one another so that these outer Gouy layers overlap, the

¹ See Svedberg: "Colloid Chemistry", p. 215.

² J. Phys., (4) 9, 457 (1910).

particles will possess an effective charge relatively to one another and consequently repel one another. But it is always conceivable that on occasion the Brownian movement may be so directed and of such intensity that the two particles might possibly touch in spite of this repulsion.

The frequency of such occurrences will be increased (i) by increasing the intensity of the Brownian movement, i.e. increasing the temperature or (ii) by decreasing the thickness of the Gouy layer (the outer Helmholtz layer) which may be accomplished by adding electrolytes to the medium or (iii) by decreasing the size of the charge on the colloidal particle, which is supposed to be caused by adsorbed electrolytic ions.

Such considerations offer a simple explanation of the experimental results recorded above. No colloidal solution will remain uncoagulated under a continuously increasing temperature. The higher the temperature the greater the molecular motion; when the motion becomes so violent that the particles are pushed into collision in spite of the electrical charge, coagulation automatically intervenes. If to the pure sol, slight traces of an electrolyte are added, the charge is reduced, the Gouy layer is depressed, collisions are not opposed by such great forces, and therefore the automatic coagulation takes place at lower temperature.

The curve given in Fig. 2 suggests a logarithmic relation between the temperature of coagulation and the concentration of the electrolyte. Attempts to get a quantitative relation between these two variables suggest the work of Arrhenius¹ and others on the relation between temperature and chemical reaction. The various suggested formulae are particular cases of a general one:

$$\frac{d \log K}{dT} = \frac{A + B T + C T^2 + \dots \text{etc.}}{T^2}$$

where T is the absolute temperature, K is the rate of a chemical reaction, and A, B, C, \dots are constants. Arrhenius' form which is the equivalent of putting all the constants except A equal to zero may be written thus:

$$K_{T_1} = K_{T_0} e^{\frac{A}{T_0 T_1} (T_1 - T_0)}$$

where the K_{T_1} and K_{T_0} are rates at temperatures T_1 and T_0 and A is a constant. Arrhenius found good agreement with this formula in testing the inversion of sugar by acids and Miyazawa's² experiments on the slow flocculation of aluminum oxide sols, agreed with the formula also. However, Arrhenius points out that in the case of ordinary chemical reaction, the increase per degree rise in temperature is very large—much larger in fact than such phenomena as that dealt with by Miyazawa. Arrhenius also shows that the increase in ordinary purely chemical actions cannot be accounted for by such physical changes as the increase with temperature in the number of collisions per second between molecules or the decrease in the viscosity.

¹ *Z. physik. Chem.*, 4, 226(1889); see Mellor: "Chemical Statics and Dynamics", 386 et seq.

² Freundlich, loc. cit., p. 465.

There are at least three distinct ways in which the increase in temperature may assist coagulation of sols such as recorded above:

(i) Increase in molecular motion, rate of diffusion, Brownian movement, viscosity, and all phenomena due primarily to molecular motion; these are all accounted for in the Smoluchowski formula for slow coagulation which shows that as far as the temperature is concerned the rate of coagulation varies as T/n where T is the absolute temperature and n is the coefficient of viscosity of the medium at the temperature T .

(ii) Since we are dealing with a phenomenon which involves electrical forces between charged bodies in a medium, the force will vary inversely as the dielectric constant of the medium—a quantity which certainly changes with temperature. The role of the dielectric constant in the action of electrolytes is most important as indicated by the work of Debye and Hückel and others. However, the experimental work on the variation of this coefficient with temperature for water does not indicate any remarkable change. The equation which has been found to hold is:¹

$$D_{T_1} = D_{T_0} [1 - \alpha(T_1 - T_0) + \beta(T_1 - T_0)^2]$$

where $\alpha = 0.0045$ and $\beta = 0.000017$. The variation given by this formula between 20°C and 180°C amounts to only 30% at the most. This 30% is a decrease in the value of the dielectric constant which means an increase in the electrical field between charged bodies in the medium—a circumstance which would tend to make the sols more stable.

(iii) The most likely change with temperature which will be effective in causing this coagulation is the change in the ionization of the water itself. Kraus² records the change in the ionization constant for water as the temperature changes in Table IV.

TABLE IV

| | | Ionization constant for water | | | | | |
|----------------------|-------|-------------------------------|------|------|------|------|------|
| Temperature | 0° | 18° | 25° | 100° | 150° | 218° | 306° |
| $K_w \times 10^{14}$ | 0.089 | 0.46 | 0.82 | 48 | 223 | 461 | 168 |

These results are plotted in the curve II of Fig. 2 which suggests a very striking relation between the change in the ionization constant and the coagulating effect of a change of temperature. However, the suggestion cannot be pressed too far, as all of these effects are undoubtedly bound up together—viz., molecular motion, viscosity, diffusion, dielectric constant, and so on.

The conclusion, however, seems to be inevitable that a sufficient rise in temperature can of itself cause the coagulation of any colloidal solution of the dispersoid type and any process of slow coagulation can be changed to rapid coagulation by a definite rise in the temperature.

¹ "Smithsonian Tables," 359 (1923).

² "Properties of Electrically Conducting Systems," 147-152.

AMMONOUS NITRIDES

(I) Ammonous Cobaltous Nitride, Ammonous Aluminum Nitride and Stannous Imide

BY F. W. BERGSTROM

Introduction: Ammonous Cobaltous Nitride

Some years ago the author prepared a bulky blue precipitate¹ approximating cobaltous amide, $\text{Co}(\text{NH}_2)_2$, in composition by pouring a liquid ammonia solution of potassium amide—a base of the ammonia system²—into a solution of cobaltous thiocyanate, the reaction proceeding in accordance with the equation, (1) $\text{Co}(\text{SCN})_2 + 2\text{KNH}_2 = 2\text{KSCN} + \text{Co}(\text{NH}_2)_2$. Rather strangely, this precipitate loses ammonia slowly and irreversibly under liquid ammonia at room temperatures, and therefore at about eight atmospheres pressure, to form black cobaltous nitride in the manner expressed by the equation, (2) $3\text{Co}(\text{NH}_2)_2 = \text{Co}_2\text{N}_2 + 4\text{NH}_3$. Since this reaction takes place much more slowly at -40° than at room temperatures, it seemed possible that cobaltous nitride might take up ammonia at still lower temperatures to form cobaltous amide in accordance with equation (2) read from right to left. However, cobaltous nitride does not appear to absorb ammonia at the temperature of an ether-carbon dioxide snow mixture.

There is a rather interesting parallelism between the properties of cobaltous amide and cupric hydroxide, for the blue cupric hydroxide slowly and irreversibly loses water at ordinary temperatures to form black products approaching cupric oxide in composition,³ just as the blue cobaltous amide loses ammonia and is converted into black cobaltous nitride. It has often been suggested³ that cupric hydroxide is a hydrous or solvovous cupric oxide, $\text{CuO} + x\text{H}_2\text{O}$, rather than a definite compound, $\text{Cu}(\text{OH})_2$. Reasoning from the analogy known to exist between the amides, imides and nitrides of the ammonia system and the hydroxides and oxides of the water system⁴ cobaltous amide should perhaps be formulated as a solvovous or ammonous cobaltous nitride, $\text{Co}_2\text{N}_2 + x\text{NH}_3$.

The present investigation was undertaken for the purpose of preparing other metallic amides and imides whose properties might allow them to be formulated as ammonous nitrides.

¹ Bergstrom: *J. Am. Chem. Soc.*, **46**, 2632 (1924).

² Franklin: *J. Am. Chem. Soc.*, **46**, 2139 (1924).

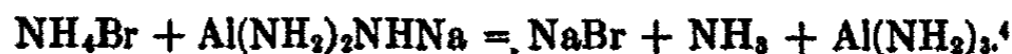
³ Van Bemmelen: *Z. anorg. Chem.*, **5**, 466 (1894); Bancroft: "Applied Colloid Chemistry," 246 (1921); Weiser: *J. Phys. Chem.*, **27**, 501 (1923), where references to the earlier literature on the spontaneous dehydration of cupric "hydroxide" are given.

⁴ Franklin: *J. Am. Chem. Soc.*, **46**, 2139 (1924); *Am. Chem. J.*, **47**, 289 (1912).

Ammonous Aluminum Nitride

The basic amides are most readily obtained by pouring a solution of potassium amide into a solution of a metallic salt in liquid ammonia. Thus, cobaltous "amide" is easily prepared by the action of potassium amide upon a solution of cobaltous thiocyanate in accordance with equation (1) just as cobaltous "hydroxide" is obtained by the action of an aqueous solution of potassium hydroxide upon a water solution of the same salt of cobalt. Attempts of Franklin¹ to prepare aluminum amide by the action of potassium amide upon a liquid ammonia solution of aluminum iodide failed because an insoluble ammonobasic iodide of aluminum was precipitated. The author found that potassium amide similarly precipitated an ammonobasic aluminum thiocyanate from a solution of aluminum thiocyanate.²

Since acids precipitate aluminum hydroxide³ from aqueous solutions of alkali metal aluminates, it is to be expected that aluminum amide would likewise be precipitated by the action of an acid upon a solution of potassium or sodium ammono aluminate, in accordance with the equation (3):



The sodium ammono aluminate required in this reaction was first made by the action of a liquid ammonia solution of metallic sodium upon amalgamated aluminum in a two-legged reaction tube, following the earlier directions of the author.⁵ The solution of sodium ammono aluminate formed in this manner was then decanted into the other leg of the reaction tube, leaving the residue of unused aluminum behind. With this solution cooled in a bath of liquid ammonia, the leg containing the residue was opened and cleaned out.⁶ Into this leg was then introduced a little less than the quantity of ammonium bromide calculated for the reaction of equation (3), after which the leg was sealed shut and the apparatus allowed to warm to room temperature. With the leg containing the ammonium bromide immersed in an ice bath and the other leg in warm water, ammonia was distilled over to form a dilute solution of ammonium bromide. This latter was poured slowly into the solution of sodium ammono aluminate in the other leg of the reaction tube until a sufficiently large precipitate of aluminum "amide" had been formed. The precipitate was washed thoroughly and then allowed to stand under pure liquid ammonia for the period of time indicated in the following table. (The figures given include the time consumed in washing the precipitate). Since aluminum "amide" reacts vigorously with water the specimens were

¹ Franklin: *J. Am. Chem. Soc.*, 27, 849 (1905).

² Prepared in anhydrous form by the action of a liquid ammonia solution of mercuric thiocyanate on aluminum.

³ A definite hydrate of Al_2O_3 is precipitated under certain conditions. Cf. Weiser, *The Hydrous Oxides*, p. 108.

⁴ Ammonium bromide behaves as an acid in liquid ammonia solution. Franklin and Kraus: *Am. Chem. J.*, 23, 305 (1900); *J. Am. Chem. Soc.*, 27, 822 (1905).

⁵ *J. Am. Chem. Soc.*, 45, 2792 (1923).

⁶ Cf. Franklin: *J. Phys. Chem.*, 15, 511 (1911).

hydrolyzed first by means of water vapor and then dissolved in dilute hydrochloric acid. Aliquot portions of this acid solution were taken for analysis. Aluminum was determined as oxide and nitrogen was estimated volumetrically as ammonia.

Analyses

| Calculated for | Dried in a vacuum at room temperatures | | | | | Found |
|----------------------------------------------------------------------------------------------------|----------------------------------------|-----------------------|-----------------------------------|------|----------------|-------|
| | Al(NH ₂) ₃ | Al(NH)NH ₂ | Al ₂ (NH) ₃ | AlN | 1 ^a | |
| Al | 36.0 | 46.5 | 54.5 | 65.9 | 40.7 | 45.2 |
| N | 56.0 | 48.2 | 42.4 | 34.2 | 52.0 | 49.0 |
| Time in days during which ppt. remained in contact with liquid ammonia, at 20°, prior to analysis. | | | | | (3-6) | 3 |
| | 3 ^a | 4 | 5 | 6 | 7 ^b | |
| Al | 50.1 | 53.1 | 55.3 | 55.2 | 55.6 | |
| N | 44.7 | 41.7 | 40.7 | 40.2 | 38.8 | |
| Time, etc. | 5 | (3-4) | 7 | 21 | 60 | |
| | Heated in a vacuum at 200-220° | | | | | |
| | 3 ^a | 4 | 7 | | | |
| Al | 55.4 | 57.2 | 56.7 | | | |
| N | 41.0 | 39.2 | 39.8 | | | |

Heated in a vacuum at 380°

No. 6, Al 58.5, N 37.8. Calcd. for AlN, Al 65.9, N 34.2.

^a Prepared from potassium ammono aluminate.

^b Found to contain 3.8 percent sodium.

Discussion—It is evident from an examination of the above table that the substances precipitated by pouring a liquid ammonia solution of ammonium bromide into a solution of sodium or potassium ammono aluminate are not constant in composition, even though some of the specimens (Nos. 1, 2, 3, 4) were prepared in almost the same manner. It was thought that the lack of agreement in the analyses might be due to the differences in purity of the preparations, but this seems improbable in view of the fact that the total amount of halogen and alkali metal present as impurities varies from a few tenths of a percent in preparations No. 1 and 2 to a little under four percent in preparation¹. One should not expect impurities in the amounts found to have such a profound influence upon the composition of the specimens. For other metallic amides which have been prepared are much more constant in composition, in spite of contamination with several percent impurity.²

Since aluminum forms very basic salts in liquid ammonia, it was thought possible that the preparations might be mixtures of highly basic aluminum

¹ These amounts were estimated roughly by comparison of the sum of the percentages of aluminum and nitrogen found with the sum of the percentages of these two elements calculated for pure compounds of Al, N and H having the same atomic proportion of nitrogen to aluminum. Preparation 7 was found on analysis to contain 3.8 percent sodium.

² For instance, manganese amide and some specimens of magnesium amide. Bergstrom: J. Am. Chem. Soc., 46, 1557 (1924); 48, 2851 (1926).

bromides or highly acidic sodium ammono aluminates¹ whose differences in composition might account for the divergent analyses. Thus, the composition of preparation 2 agrees approximately with the formula $\text{Al}(\text{NH})\text{NH}_2$, or for that matter with the general formula $\text{Al}(\text{NH})\text{NH}_2 \cdot \text{NaNH}_2$, where x is sufficiently large (about 15). No. 7, the least pure specimen, has the approximate composition $4\text{Al}_2(\text{NH})_3 + 4\text{AlN} + \text{NaNH}_2$, since the impurity is chiefly sodium. Thus, in preparation 2, sodium amide is in combination with 15 molecules of $\text{Al}(\text{NH})\text{NH}_2$ and in preparation 7 with 4 molecules each of $\text{Al}_2(\text{NH})_3$ and AlN . If these acidic aluminates are definite compounds, one certainly should not expect such a variation in the composition of the aluminum-containing portion of the molecule. Moreover, the existence of amorphous compounds of such molecular complexity is very improbable. It is more reasonable to consider that the preparations contain different amounts of adsorbed impurity.

Now the specimens, dried in a vacuum at room temperatures change in composition from No. 1, an aluminum amide which has lost almost enough ammonia to form aluminum imide-amide, $\text{Al}(\text{NH})\text{NH}_2$, to Nos. 6 and 7, which appear to be partially deammonated aluminum imides, $\text{Al}_2(\text{NH})_3$. These differences in composition do not completely disappear even when the preparations are heated in a vacuum above 200° . It would seem in view of the facts enumerated above that the preparations cannot be regarded as definite compounds. It is suggested that they be considered solvates or ammonous aluminum nitrides in the sense that ferric and cupric hydroxides are considered hydrous oxides, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and $\text{CuO} \cdot x\text{H}_2\text{O}$.

There are indeed many points of similarity between the hydrous oxides and the substances we regard as ammonous cobaltous nitride and ammonous aluminum nitride. The water content of the hydrous oxides as well as the ammonia content of these ammonous nitrides depends upon the previous history of the specimens. Some hydrous oxides, as for instance hydrous cupric oxide, change into the corresponding oxide under liquid water at ordinary temperatures,² just as cobaltous "amide" changes to cobaltous nitride under liquid ammonia. Ammonous aluminum nitride appears to lose ammonia very slowly in this manner. Thus, preparations 7 and 6, which were washed and kept under liquid ammonia respectively two months and three weeks prior to analysis contain less nitrogen than the other specimens. The change of the blue gelatinous cupric "hydroxide" into cupric oxide may be prevented or greatly retarded by the presence of adsorbed salts or metallic hydroxides.² It is possible that the differences in the composition of the specimens of ammonous aluminum nitride may in part be due

¹ Basic salts may be represented for purposes of convenience as double compounds of the normal salt with the corresponding base. Thus, the insoluble ammonobasic aluminum iodide prepared by Franklin (*J. Am. Chem. Soc.*, 37, 847 (1915)) may be written as $3\text{Al}(\text{NH}_2)_2 \cdot \text{AlI}_3 \cdot 6\text{NH}_3$. Similarly we can represent an ammono "basic" sodium aluminate as the double compound $\text{Al}(\text{NH}_2)_2 \cdot \text{NHNa} \cdot x\text{Al}(\text{NH}_2)_3$, or more simply as $\text{NaNH}_2 \cdot x\text{Al}(\text{NH}_2)_3$. Perhaps it would be more logical to call such substances ammono acidic aluminates, since the amphoteric base aluminum amide has certainly acted as a weak acid in the formation of sodium ammono aluminate.

² Weiser and others: *loc. cit.*

to varying amounts of adsorbed impurities. It was indeed found that potassium amide reacts with or is adsorbed by solvous aluminum nitride¹. It is impossible to remove this potassium amide by continued washing.

The vapor pressure-composition curve for a hydrous oxide at constant temperature shows no break which would indicate a definite hydrate. Similarly, the vapor pressure-composition curve of the system AlN-NH_3 should show no break corresponding to a definite ammonate of aluminum nitride. In the present work no definite decomposition pressures were observed when specimens of ammonous aluminum nitride were heated in a vacuum, possibly because equilibrium between gas and solid is reached so slowly. A determination of the pressure-composition curve of the system AlN-NH_3 at a series of temperatures is now in progress in this laboratory.²

Many nitrides prepared in liquid ammonia and dried in a vacuum at room temperatures retain small quantities of ammonia which are given off on heating at a higher temperature. Thus, ferrous, cobaltous and nickelous nitrides give off small quantities of ammonia in a vacuum at 100° . It is probable that the liberated ammonia is not ammonia of constitution but ammonia held in the same manner that water is held in the hydrous oxides.

Other Properties of Ammonous Aluminum Nitride.—Ammonous aluminum nitride reacts with solutions of an excess of potassium amide or ammonium bromide to form respectively potassium ammono aluminate and aluminum bromide. Ammonous aluminum nitride in ammonia, like aluminum hydroxide in water, reacts with or adsorbs alizarin with the formation of a colored lake.³ The lake formed by the action of the purplish solution of alizarin in liquid ammonia upon aluminum amide is less stable toward washing than the corresponding lake formed in water. As alizarin contains four atoms of oxygen, it was thought possible that the ammonous aluminum nitride might have been converted to aluminum hydroxide, which would then unite with alizarin to form a lake. It was found that very little if any of the ammonous aluminum nitride was converted to hydroxide by the alizarin, since the lake reacted with water as if it contained $\text{AlN} + x\text{NH}_3$, and since the ratio of Al:N in the precipitate was about what one would expect for a pure ammonous aluminum nitride which had remained in contact with liquid ammonia for the same length of time as the lake.

It was thought possible that an ethyl derivative of aluminum amide, ethyl ammono aluminate, might be prepared by the action of ethyl iodide

¹ An excess of potassium amide dissolves ammonous aluminum nitride to form potassium ammono aluminate. On the other hand, potassium amide reacts with a large excess of ammonous aluminum nitride to form insoluble compounds, or more probably soluble substances which are subsequently adsorbed.

² The failure to obtain a constant pressure corresponding to the equilibrium between a nitride and ammonia gas may not prove that the substance under consideration is an ammonous nitride. Thus it has been found that the deammonation of barium and calcium amides to the corresponding nitrides at elevated temperatures is irreversible. (Kraus: J. Am. Chem. Soc., 45, 2559 (1923). Nevertheless, there can be no doubt of the existence of either calcium or barium amide, for these substances are constant in composition over such a wide range of temperature.

³ This lake is a lighter red than the corresponding water lake.

on a liquid ammonia solution of sodium ammono aluminate, in accordance with the equation, $\text{Al}(\text{NH}_2)_2\text{NHNa} + \text{C}_2\text{H}_5\text{I} = \text{NaI} + \text{Al}(\text{NH}_2)_2\text{NHC}_2\text{H}_5$. The white flocculent precipitate obtained in this reaction was found to be impure ammonous aluminum nitride, signifying that the expected ester was formed and then underwent ammonolysis in accordance with the equation, $\text{Al}(\text{NH}_2)_2\text{NHC}_2\text{H}_5 + \text{NH}_3 \rightarrow \text{C}_2\text{H}_5\text{NH}_2 + \text{Al}(\text{NH}_2)_3 \rightarrow \text{C}_2\text{H}_5\text{NH}_2 + \text{AlN} + \text{XNH}_3$.

Stannous Imide, SnNH , and Stannous Nitride, Sn_3N_2

In view of the fact that ammonous aluminum nitrides are prepared by the action of ammonium bromide upon a solution of sodium or potassium ammono aluminate in liquid ammonia, it was thought that a stannous amide, imide or an ammonous stannous nitride might be prepared by the action of ammonium bromide upon a solution of potassium ammono stannite in accordance with the equation, (4) $\text{SnNK} + \text{NH}_4\text{Br} = \text{SnNH} + \text{NH}_3 + \text{KBr}$. It was found that this reaction takes place readily.

Preparation 1. Potassium ammono stannite was first prepared by the action of a solution of potassium amide in liquid ammonia upon stannous chloride in slight excess of the amount required by the equation, (5) $\text{SnCl}_2 + 3\text{KNH}_2 = \text{SnNK} \cdot 2\text{NH}_3 + 2\text{KCl}$.¹ One leg of the reaction tube used now contained a solution of potassium ammono stannite together with a precipitate of the sparingly soluble potassium chloride and the unused stannous chloride. The other leg of the reaction tube which contained the small tubes from which the potassium had dissolved together with the iron wire catalyst used in the conversion of the alkali metal solution to potassium amide, was opened, cleaned out and resealed.² Into this clean leg was then decanted the solution of potassium ammono stannite. Now with this solution cooled to -40° , the leg containing the residual potassium chloride was opened, cleaned out and resealed after introducing enough ammonium bromide for the reaction of equation (4). Stannous imide was obtained as a brown amorphous precipitate by slowly pouring a diluted solution of ammonium bromide into the solution of potassium ammono stannite. After a thorough washing with liquid ammonia the stannous imide was heated in a vacuum, hydrolyzed with water and then dissolved in dilute hydrochloric acid preparatory to analysis. Tin was determined as oxide after previous precipitation as sulfide. Potassium was recovered as sulfate from the filtrate of the stannous sulfide to which sulfuric acid had been added. Nitrogen was estimated volumetrically as ammonia. Subs. dried in a vacuum at 20° , 0.5167 g; heated in a vacuum at 170° , 0.5140 g. One quarter gave 0.1448 g. SnO_2 and one half gave 0.02630 g. nitrogen.

¹ The very slightly soluble stannous chloride first reacts with potassium amide to form the almost insoluble stannous imide, in accordance with the equation, $\text{SnCl}_2 + 2\text{KNH}_2 = \text{SnNH} + \text{NH}_3 + 2\text{KCl}$. Potassium amide dissolves the amphoteric base stannous imide to form potassium ammonostannite, in the manner represented by the equation, $\text{SnNH} + \text{NH}_3 + \text{KNH}_2 = \text{SnNK} \cdot 2\text{NH}_3$, Bergstrom: J. Phys. Chem., 30, 15 (1926).

² Cf. Franklin: J. Phys. Chem., 15, 511 (1911).

Preparation 2. Subs. dried in a vacuum at 20°, 0.2690 g; heated in a vacuum at 200°, 0.2653 g. One half gave 0.1470 g. SnO₂ while the other half gave 0.0128 g. nitrogen.

Preparation 3. Subs. dried in a vacuum at 20°, 0.2917 g; heated in a vacuum at 170°, 0.2890 g; heated in a vacuum at 220°, 0.2876 g. One half gave 0.1608 g. SnO₂. One half gave 0.01423 g. nitrogen.

Preparation 4. Subs. dried in a vacuum at 20°, 0.3700 g; heated in a vacuum at 175°, 0.3663 g. One quarter gave 0.1021 g. SnO₂ and one half gave 0.01755 g. nitrogen.

Preparation 5. Subs. dried in a vacuum at 20°, 0.3133 g; heated in a vacuum at 180°, 0.3094. One half gave 0.1711 g. SnO₂ and the second half gave 0.01441 g. nitrogen.

Preparation 6. In this experiment, stannous imide was heated to a temperature of 340° in a vacuum for the purpose of preparing stannous nitride, Sn₂N₂. The product so obtained was not dissolved by the prolonged action of hot solutions of hydrochloric acid or sodium hydroxide, proving therefore to be much more inert than stannous imide, which reacts with water with a slight evolution of heat and dissolves fairly readily in dilute hydrochloric acid.

For the purpose of analysis, the stannous nitride was removed from the reaction tube in suspension in dilute hydrochloric acid and treated with hydrogen sulfide to precipitate a small amount of dissolved tin. The combined precipitates of stannous nitride and sulfide were fused with a mixture of sodium carbonate and sulfur. Tin sulfide was precipitated by acidifying the water solution of this fusion. Subs. dried in a vacuum at 115°, 0.4066; heated in a vacuum at 340°, 0.3894 g. The entire specimen gave 0.4546 g. SnO₂.

Summary of Analyses

Heated in a vacuum at 150°-200°

| Calculated for SnNH | | Found | | | | | |
|---------------------|------|-------|------|------|------|------|------|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| Sn | 88.8 | 88.8 | 87.3 | 88.1 | 87.8 | 87.1 | 88.1 |
| N | 10.5 | 10.2 | 9.6 | 9.6 | 9.6 | 9.3 | — |

Heated in a vacuum at 340°, No. 6, Sn 92.0. Calculated for Sn₂N₂, Sn 92.7.

The preparations are all contaminated with small quantities of potassium and halogen. For this reason, the analyses do not agree as closely with the calculated composition of SnNH as might be desired. In view of the constancy in composition of the preparations it is possible that stannous imide is a definite compound and not an ammonous stannous nitride. The question then naturally arises as to whether the small additional amount of ammonia retained by stannous imide at room temperatures is constitutional ammonia, in the form of stannous amide, or adsorbed ammonia. If the latter, it would be necessary to postulate the existence of an ammonous stannous imide, if we assume that the imide is itself a definite compound.

Other Properties of Stannous Imide. Like many compounds of the ammonia system, stannous imide is hydrolyzed by water to ammonia and the corresponding compound of the water system, hydrous stannous oxide or stannous hydroxide. Like the latter stannous imide is an amphoteric base, for it dissolves in a liquid ammonia solution of the base potassium amide to form potassium ammono stannite, and in a solution of the acid, ammonium thiocyanate, to form a soluble thiocyanate of tin.

Potassium ammono stannite may be nitridized to potassium ammono stannate just as potassium aquo stannite is oxidized to an aquo stannate. Thus, crystals of the sparingly soluble potassium ammono stannate, $\text{Sn}(\text{NK})_2 \cdot 4\text{NH}_3$,¹ are obtained when iodine is added to a liquid ammonia solution of potassium ammono stannite containing an excess of potassium amide², the reaction proceeding in accordance with the equation, $\text{SnNK} + 2\text{I} + 3\text{KNH}_2 = \text{Sn}(\text{NK})_2 + 2\text{KI} + 2\text{NK}_3$. Found, Sn 39.2, N 26.3. Calculated for $\text{Sn}(\text{NK})_2 \cdot 4\text{NH}_3$, Sn 40.5, N 28.7. The specimen is thus an impure potassium ammono stannate.

A solution of metallic potassium in liquid ammonia reduces potassium ammono stannite to a soluble potassium tin alloy, K_xSn_x , which contains the tin in the anion³. The reduction has therefore proceeded beyond the stage of metallic tin.

In conclusion, the author wishes to thank Dr. E. C. Franklin for his interest in this work.

Summary

(1) In order to explain certain anomalous properties of cobaltous amide it has been suggested that this substance is an ammonous cobaltous nitride, $\text{Co}_2\text{N}_2 + x\text{NH}_3$, an ammonia analogue of the hydrous oxides.

(2) It was not found possible to precipitate an aluminum amide, imide, or nitride of definite composition from a liquid ammonia solution of sodium or potassium ammono aluminate. Since the precipitated substances, under comparable conditions, contain from 40.7 to 55.6 percent aluminum and 38.8 to 52.0 percent nitrogen with very little alkali metal or bromine as impurity, it is suggested that they be regarded as ammonous aluminum nitrides, $\text{AlN} + x\text{NH}_3$.

(3) The small amount of ammonia frequently retained by many nitrides prepared in liquid ammonia is perhaps bound in the same manner as the ammonia in $\text{Co}_2\text{N}_2 + x\text{NH}_3$ or $\text{AlN} + x\text{NH}_3$.

(4) Stannous imide, SnNH , and stannous nitride, Sn_2N_2 , have been prepared. Stannous imide may be a definite compound and not an ammonous stannous nitride.

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¹ Fitzgerald: J. Am. Chem. Soc., 29, 1692 (1907).

² At -40° .

³ J. Am. Chem. Soc., 44, 1221 (1922); J. Phys. Chem., 30, 15 (1926).

22-14

THE SORPTION OF WATER VAPOUR BY ACTIVATED CHARCOALS
PART. I. APPARATUS—TECHNIQUE—NATURE OF
CHARCOALS USED

BY P. G. T. HAND AND D. O. SHIELDS

1. Introduction

The work to be described in this, and succeeding papers forms part of an investigation carried out in this laboratory under the direction of Professor A. J. Allmand from the commencement of 1921, and still in progress. Its primary purpose has been the establishment of the experimental facts concerning the sorption of vapours by charcoal with a view, of course, of arriving at an understanding of the essential nature of the phenomenon, and of an explanation of the marked differences shown between the behaviour of the vapours of water and of other substances. In addition, whatever the use adsorbent charcoals may be put to, the omnipresence of water vapour makes a study of its sorption relations, in particular, of direct practical importance.

When this work was commenced, the only previous publications on water vapour of importance known to us were those of Schmidt and Hinteler,¹ Bachmann,² and Lowry and Hulett.³ During the course of the work, there have been published or become available to us papers by Rakovsky,⁴ Gustafson,⁵ Hällstrom,⁶ Berl and Andress,⁷ Isobe,⁸ Gustaver,⁹ Katz¹⁰ and Coolidge.¹¹

Two general experimental methods have been employed. In the one ("dynamic" or "streaming" method), a current of air or of nitrogen charged with a known partial pressure of water vapour, by bubbling through sulphuric acid solutions of definite concentrations at 25°C, was passed through a column of charcoal contained in a silica tube at 25°C ± 0.05° until constancy of weight had been reached. The charcoal had been previously outgassed at a definite temperature, and subsequently saturated with the pure dry gas at 25°C. The purpose of the experiments in the nitrogen stream was to investigate whether or not the presence of oxygen in charcoal has a specific effect on the sorption process.

In the second ("static" or "vacuum") method of experimentation, water vapour, free from any admixed gas, was admitted to the previously evacuated

¹ Z. physik. Chem., 91, 103 (1916).

² Z. anorg. Chem., 100, 1 (1917).

³ J. Am. Chem. Soc., 42, 1393 (1920).

⁴ J. Russ. phys. Chem. Soc., 49, 371 (1917).

⁵ Arkiv. Kemi. Mineral Geol., 7, No. 22, 1 (1919).

⁶ Dissertation Helsingfors (1920).

⁷ Z. angew. Chem., 34, 369 (1921).

⁸ Eng. Chem. J. (Japan), 1, 99 (1921).

⁹ Kolloidchem. Beihefte, 15, 185 (1922).

¹⁰ Proc. Amsterdam Acad., 26, 548 (1923).

¹¹ J. Am. Chem. Soc., 46, 596 (1924).

charcoal (contained, as before, in a silica or glass tube at 25°C), and the change in weight determined when the pressure, read off on a mercury manometer, had become constant. A series of such experiments, by either method, extending from zero water vapour pressure up to saturation at 25°C enabled the sorption isotherm to be plotted. In almost all cases these isotherms were determined with falling as well as rising water vapour pressure, i.e. *desorption* as well as sorption isotherms were investigated. In a few cases (with the "static" method) experiments were made at temperatures other than 25°C .

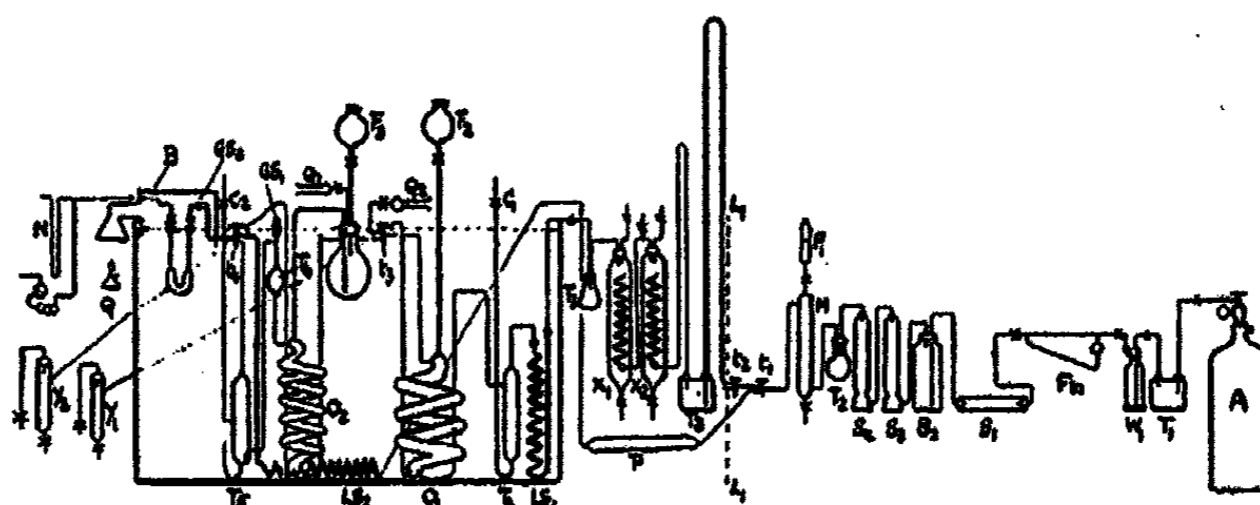


FIG. 1a

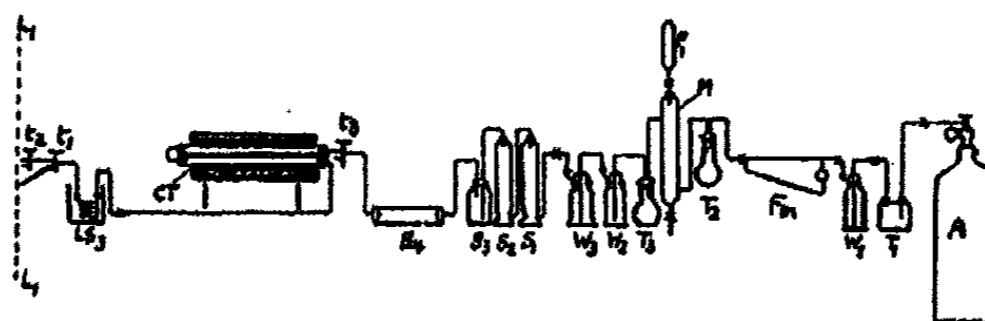


FIG. 1b

2. Dynamic Experiments

The main apparatus for the air stream experiments is shown in Fig. 1a, while the necessary modifications for working in nitrogen are seen in Fig. 1b. As certain details of the procedure in the two cases differ it will be as well to describe first those items which are common to both methods.

(a) **Charcoal tube:** The charcoal is contained in a silica U, Fig. 2 C, fitted with glass L pieces ground at each end ($g_1 g_2, g_3 g_4$). The former fit the U by means of silica grindings surmounted by cups $W_1 W_2$ (filled with Everett's vacuum wax). The taps are well-ground vacuum taps lubricated with Ramsay grease.

(b) **Evacuation of charcoal:** the U containing the charcoal is heated in an electric furnace so arranged that the arms of the U project about 5 cms. from the furnace. The wax seals are protected by a thick asbestos sheet, and asbestos wool packing (*vide* Fig. 3A (e)). g_3 and g_4 fit into ground cups of the evacuation leads, and the joints are made tight by vacuum wax. The evacua-

ation outfit consisted of a Kraus mercury vapour pump backed by a Cenco Hyvac Oil Pump. Pressures are measured by means of a McLeod gauge, inserted in the evacuation lines. In most of this work two evacuation temperatures are used viz. 270°C and 800°C .

(c) Vacuum weight of charcoal: In determining this the usual precautions are taken to check the volume of the empty container by filling with mercury at a known temperature and weighing; checking for the free-space air over the charcoal which necessitated determining the density of the charcoal, reference to which will be made later, and also determining the loss in weight of the charcoal during evacuation. All weighings are carried out with a U-tube counterpoise. The weights used were checked by means of the Kohlrausch method.

(d) Saturation of charcoal with dry gas: This is carried out by attaching the U to the ground cup GS_2 Fig. 1a, allowing the contents to come to the temperature of the thermostat and then passing a stream of dry gas over the charcoal at a rate of 60-80 ccs. per min. Equilibrium being judged to be set up when the change in weight of the U was not greater than ± 0.1 mgr. Knowing the free-space volume above the charcoal, a correction for the amount of gas in this was made, and hence the weight of the sorbed gas obtained.

(e) Experimental details using an air stream:

(1) Dry Air: Air from cylinder A Fig. 1a is passed through trap T_1 to the gas washer W_1 , containing conc. sulphuric acid and thence by way of flowmeter Fm to the soda lime train S_1 , S_2 , S_3 and S_4 . The rate of flow is roughly adjusted by means of the reducing valve fitted to the cylinder, and finally adjusted by taps between W_1 and A. Leaving S_4 the air passes via trap T_2 through a sulphuric acid pumice tower M , filled from F_1 , and finally, via two-way tap t_1 over phosphorus pentoxide, contained in P , into the thermostat by way of lead coil LS_2 to two-way tap t_4 ; finally issuing at GS_2 . The U is attached at this point by means of g_3 , Fig. 2c, and connected to a mercury manometer N from g_4 by means of rubber tubing. By carefully opening the container taps the flow of air is admitted to the charcoal. The manometer is used to ascertain the excess pressure, over atmospheric, of the air in the free space. Usually 2-3 mms.

Dryness of Air: In order to obtain perfectly dry air two extra gas bubblers containing conc. sulphuric acid were introduced between S_4 and T_2 Fig. 1a. To check the dryness of the air a stream at 100 cc. per min. was passed through the apparatus and thence over a weighed quantity of pure phosphorus pentoxide contained in a U-tube fitted with ground-in glass tap heads, connected of course to GS_2 . The exit side of the U was connected to an absorption bulb containing conc. sulphuric acid.

After two hours the U-tube, weighed against a counterpoise, shewed no increase in weight.

Purity of air: This was tested by attaching a small bubbling apparatus, containing lime water to GS_2 , and passing air through the train at 100 ccs. per min. for a number of hours. No precipitate of calcium carbonate was observed.

(2) Air charged with water vapour: In this case the air-stream is diverted at two-way tap t_1 via two-way t_2 through trap T_2 , containing a shallow layer of conc. sulphuric acid, into which dips a capillary inlet tube, and thence to the glass coil saturators X_1 and X_2 . These saturators are filled with sulphuric acid solutions of such strength that a water vapour pressure is obtained of approximately 1 mm. below the vapour pressure of the acid solutions of the saturators situated within the thermostat. Leaving the two "external" saturators the moist air travels through the "splash catcher" T_3 , through the lead coil LS_1 , to the "internal" glass coil saturator O_1 by way of safety trap T_4 . From O_1 the air stream passes by way of two-way tap t_3 into the "internal" saturator O_2 , and thence by way of traps T_5 and T_6 , through two-way tap t_4 to GS_2 , where it enters the charcoal tube. The two internal saturators are filled with sulphuric acid of predetermined strength to give a known water vapour pressure at 25°C .

The volumes of X_1 and X_2 are both 2000 cc., while O_1 contains 400 cc. of acid, and O_2 125 cc.

During any run with moist air the parts of the U exposed above the water level, indicated by a dotted line, are kept at $26^\circ\text{C} \pm 1^\circ\text{C}$ by means of a metal box, B, which is heated from below by means of a micro burner Q.

Efficiency of Saturators: In order to determine whether the air leaving the final saturator O_2 was saturated with respect to the solution contained therein, the amount of water sorbed by the charcoal for a given solution was determined. An additional saturator, Fig. 2D, was introduced after O_2 . The U-tube containing the evacuated charcoal, after saturation with dry air, was connected to the extra saturator and air again passed over the charcoal via the saturating train and the extra saturator. The value thus obtained for the weight of water sorbed agreed very well with the value obtained without the extra saturator.

| Pressure water vapour | Mgs/grm water sorbed | |
|-----------------------|----------------------|--------------|
| | 4 saturators | 5 saturators |
| 13.40 mms | 156.49 | |
| 13.36 mms | | 156.38 |

Completeness of the saturation of dry air with respect to the solution through which it passed is confirmed by the very small change in concentration of sulphuric acid after passage of air for many hours.

| Run No. | Hrs. of passage of air | Concentration of Solution % H_2SO_4 |
|---------|------------------------|--------------------------------------------------------|
| 1 | 0 | 40.13 |
| | 24 | 40.09 |
| 2 | 0 | 37.01 |
| | 25 | 36.99 |
| 3 | 0 | 30.94 |
| | 127 | 30.96 |

(3) Determination of water vapour pressures: The vapour pressures of the solutions were determined from a concentration-pressure curve plotted from the data of Regnault and Sorel.¹ The concentrations of the solutions were determined by means of density measurements using a 10 cc. pycnometer which was weighed against a sealed counterpoise. Two determinations for each solution being made, agreement being within 0.5 mgr. The concentrations were obtained from Domke's² figures, plotted as a concentration-density curve

(4) Possible carriage forward of sulphuric acid: Small quantities of sulphuric acid will, no doubt, be carried over to the charcoal in the course of time. To test this, a stream of air was passed through the saturators at 80 cc. per min., and thence into a flask containing 150 cc. 1 N BaCl₂. After 5 hours a very faint turbidity was observed. A check solution containing 1.5×10^{-4} gm 98% H₂SO₄ in 150 cc. 1 N BaCl₂ gave a readily noticeable precipitate. By comparison it was estimated that the turbidity in the test run represented less than 5×10^{-6} gm H₂SO₄. This turbidity was obtained after passage of air through 61% sulphuric acid solution (the most concentrated solution used). Generally speaking, the time of streaming through the more concentrated solutions is much less than in the case of the weaker solutions. Equilibrium being more rapidly obtained at low vapour pressures than at higher ones; so that the average amount of acid carried over could not be greater than about 1×10^{-6} gm H₂SO₄ per hour. As some charcoals were exposed to various humid streams for 600 hours the maximum quantity of acid carried over would not be greater than 6×10^{-3} gm, or for a charge of 3 gms charcoal 2 mgr/gm.

(5) Changing saturating solutions: The saturators O₁ and O₂ are completely filled with the required solution from F₂ and F₃. The solutions are then drawn off through Y₁ and Y₂, well mixed and the process repeated, after which the saturators are filled to the required height. The traps T₄, T₅ and T₆ are washed, three times, by blowing over solution from O₁ and O₂, making use of soda-lime tubes Q₁ and Q₂ to prevent contamination with carbon dioxide. Withdrawal of the washings is effected via C₁ and C₂, which are finally sealed after leaving a small quantity of liquid at the bottom of T₄ and T₅.

(f) Experimental details using a nitrogen stream.

(1) Dry Nitrogen: The apparatus used in the nitrogen stream experiments is shown in Fig. 1b. The dotted line L₁ L₁ denotes the line of demarcation to the left of which the apparatus is similar, except for a few minor details, to the air stream apparatus. Nitrogen is obtained from Cylinder A, and is 99.5% pure. The usual traps, gas washer, flow meter, and pumice-sulphuric acid tower are present. (T₁ W₁, Fm and M). T₂ is a trap while W₂ and W₃ contain conc. sulphuric acid. S₁, S₂, S₃ and S₄ constitute the sold lime train. From S₄ the dry nitrogen passes over a mixture of electrolytic

¹ Landolt-Börnstein: "Tabellen," 426-427 (1912).

² Landolt-Börnstein: "Tabellen," 265-266 (1912).

copper foil, and copper wire gauze (60 mesh) contained in two combustion tubes, CT, inserted in an electric furnace maintained at 400°-450°C. This acts as the deoxidizer. Leaving this the gas flows through the cooling coil LS₂, and passes by way of two-way tap t₁ to the phosphorus pentoxide tube, through the thermostat, to the U tube. In order to work in as pure a nitrogen stream as possible, a special attachment to the ground joint connection GS₂ was used where by the dead space between the inserted limb of the U-tube and tap t₄, Fig. 1a, could be evacuated and flushed out with the pure gas before it was allowed to flow over the charcoal. This procedure was carried out every time the U-tube was attached to the apparatus.

Purity of Oxygen: To test the amount of oxygen present in the gas stream, a method was worked out for the estimation of small amounts of oxygen in gaseous mixtures.¹ The point of attachment of this apparatus to the streaming apparatus is not shewn in the diagram Fig 1a.

A large number of tests were carried out on the dry nitrogen stream; results showed that the amount of oxygen present was of the order of less than 1 part in 1.5×10^5 by volume.

Dryness of Nitrogen: This was tested in exactly the same manner as in the air stream method; after 8 hours run at 80 ccs. per min. no increase in the weight of the P₂O₅ tube could be detected.

(2) Nitrogen charged with water vapour: In this case the flow of gas is diverted at t₁ (Fig. 1b) through t₂ to the usual saturation line as shewn in Fig. 1a.

Purity of Nitrogen charged with water vapour: A few of the tests taken on the moist gas are as follows:

(1) Fresh charge of copper in deoxidizer (100 gms). Freshly made up acid. Apparatus swept out with nitrogen for 2 hours, copper not heated. After flowing for $\frac{1}{2}$ hour over copper at 400°-450°C. Oxygen detected: 1 part in 1.4×10^4 parts N₂.

(2) Fresh charge of copper in deoxidizer. Freshly made up acid. Apparatus swept out with nitrogen for 2 hours, copper not heated. After flowing $1\frac{1}{2}$ hours over heated copper.

Oxygen detected: 1 part in 6.6×10^5 parts N₂.

| Time of flow N ₂ over deoxidiser Hrs. | Oxygen detected | Rate of flow ccs./min. |
|--------------------------------------------------------|----------------------|---------------------------|
| 100 | 1/ 1.4×10^4 | 70-80 |
| 140 | 1/ 1.4×10^4 | 70-80 |
| 160 | 1/ 1.4×10^4 | 70-80 |

In many instances 100-200 hours elapsed before the charcoal reached equilibrium. To keep the oxygen concentration down to the limits found in the foregoing tests the deoxidizer was recharged every 60-100 hours. It would therefore be safe to assume that the maximum concentration of oxygen present is not greater than $1/1.4 \times 10^4$.

¹ Hand: J. Chem. Soc., 123, 2573 (1923).

(g) Record of a typical run: To obtain data to plot the results as an isotherm an experiment must be composed of a number of "runs." that is, a series of determinations of equilibrium points for various partial pressures of water vapour.

In the cases where the velocity of sorption was fairly rapid, i.e. at low pressures, the stream was passed over the charcoal until no change in the quantity of water sorbed took place over a fairly lengthy period, usually 5-7 hours. In the case of runs taking 200 hours or so equilibrium was judged when the change in weight was not greater than 0.1 mgr/gm per hour. As an example of how a "run" is carried out the following figures, taken from a trial run, will make clear the main details.

| | |
|----------------------------------------|-----------------------|
| Stream: | Nitrogen—water vapour |
| Charcoal: | American coconut. |
| State of Charcoal: | As taken from stock. |
| Mesh size: | 10-12. |
| Temp. of outgassing: | 800°C. |
| Evacuated Wt. of charcoal: | 1.3754 gms. |
| Evacuated Wt. of container + charcoal. | 2.1526 gms. |
| Internal vol. of U-tube: | 14.63 ccs. |

(1) Saturation with dry Nitrogen.

| 1 Hrs. | 2 Rate ccs/min | 3 Press N ₂ mm | 5 Wt. of N ₂ in free space gms. | 6 Wt. of U + contents gms. | 7 Wt. of N ₂ sorbed gms. |
|-----------|----------------------|---------------------------------|-----------------------------------------------------|-------------------------------------|----------------------------------------------|
| 22½ | 50 | 775.5 | 0.0158 | 2.1996 | 0.0312 |

(2) Water vapour pressure. 14.08 mms.

| 1 Hrs. | 2 Rate ccs/min | 3 Total Press. mm | 4 Press. N ₂ mm | 5 Wt. of N ₂ + Water Vap. in freespace gms | 6 Wt. of U contents gms | 7 Wt. of water sorbed. gms |
|-----------|----------------------|----------------------------|----------------------------------|----------------------------------------------------------------|----------------------------------|-------------------------------------|
| 0.75 | 75 | 752.0 | | | 2.3920 | |
| 5.5 | 70 | 752.0 | | | 2.4188 | |
| 47.5 | 70 | 753.5 | | | 2.5023 | |
| 24 | 70 | 762.3 | | | 2.5123 | |
| 22.5 | 70 | 764.5 | | | 2.5165 | |
| 16 | 70 | 762.4 | 748.32 | 0.01544 | 2.5184 | 0.3191 |
| 22.5 | 60 | 762.0 | 747.92 | 0.01543 | 2.5199 | 0.3206 |

138.75 Wt. of water absorbed = 233.15 mgs/grm.

In the above table:

Column 1 refers to the times of exposure of the charcoal to the flow of gas.
 " 2 indicates the rate of flow of the gas.
 " 3 shows the total pressure over the charcoal at the moment of detachment of the U-tube, prior to weighing.

- “ 4 gives the partial pressure of the nitrogen over the charcoal.
 “ 5 shews the weight of nitrogen + water vapour in the free space of the U-tube.
 “ 6 gives the weight of the U-tube + its contents, as weighed against its counterpoise.
 “ 7 gives the weight of water vapour sorbed by the charcoal, on the assumption that none of the gas originally present has been displaced.

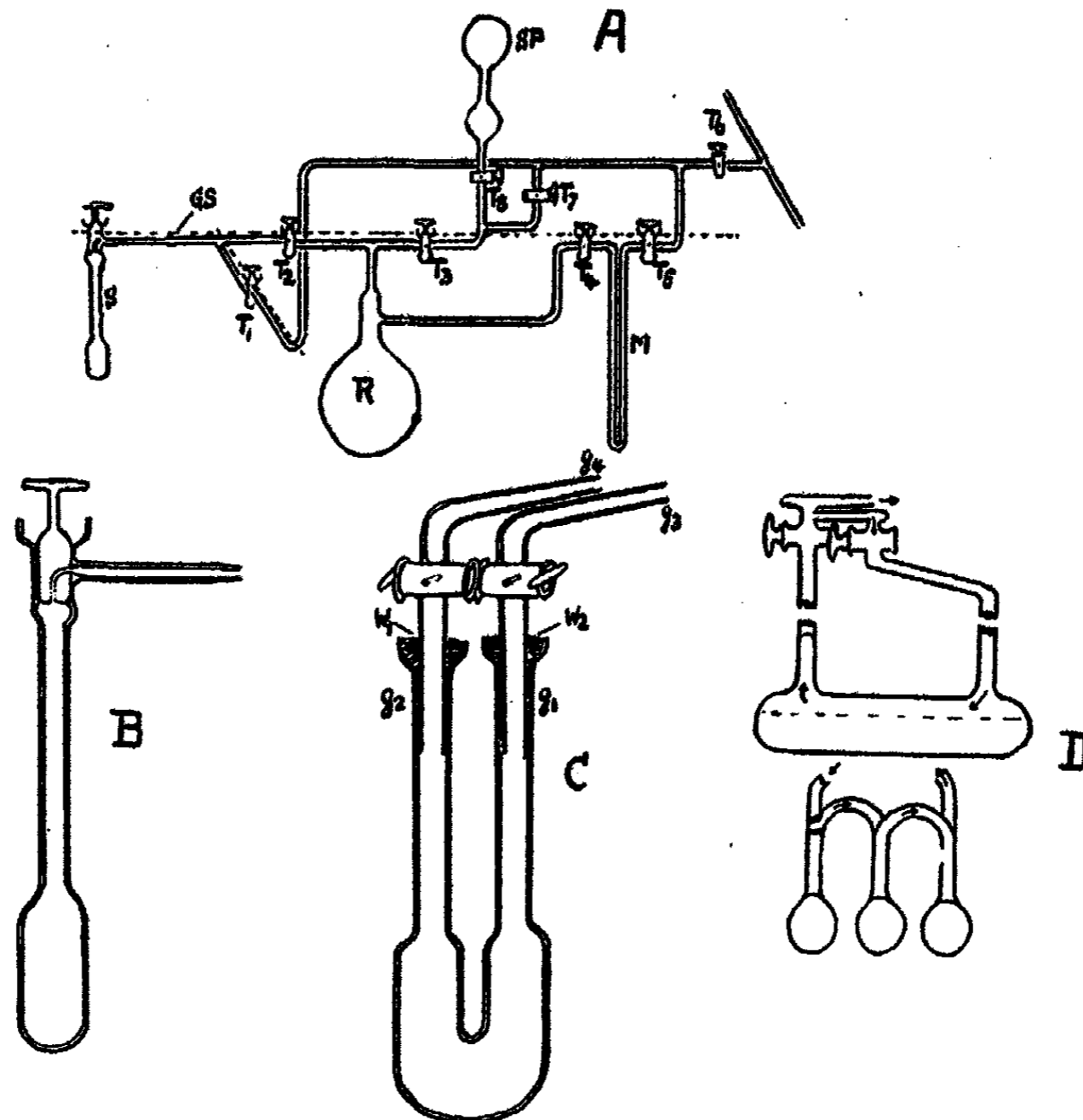


FIG. 2

3. Static Experiments

(a) Charcoal tube: The container (Fig. 2B), either silica or glass, consists of a bulb 8 cc. capacity, a well-fitting end on vacuum tap, and a side tube ending in a ground joint.

(b) Vacuum weight of charcoal: The method of obtaining the evacuated weight of the charcoal is very similar to the method used in the streaming method. A more detailed account here will suffice for both methods, static and streaming.

The container, with tap in position, and shut off, is weighed, using a sealed counterpoise of the same material and having an external volume to within 1 cc. of the container. The charcoal is introduced, the tap replaced in the shut position, and the whole reweighed. Next the container tap is greased, and inserted in the shut position and the whole reweighed. An example will shew the idea of the method.

| Charcoal | American Coconut |
|------------------------------------------------------|------------------|
| Density (after 800°C Evacuation) | 1.636 |
| Internal Volume of container No. 1 (silica) | 9.929cc |
| 1. Wt. of container + air + charcoal | = 5.2943 gms |
| 2. " " " + air | = 2.5635 " |
| (1)-(2) = Approximate Wt. of Charcoal | = 2.7308 " |
| Volume of charcoal = 1.669 cc. | |
| 3. Wt. of air in container | = 0.01172 gm. |
| T. = 17.5°C. Bar. = 740.1 mm. | |
| 4. Wt. of air in free space above charcoal | = 0.00973 " |
| T. = 18.0°C. Bar = 740.1 mm. | |
| (1)-(4) = Wt. of container + charcoal | = 5.2846 " |
| (2)-(3) = " " " | = 2.5518 " |
| 5. Unevacuated Wt. of charcoal | = 2.7328 " |
| After Evacuation. | |
| 6. Wt. of container + charcoal (after evacuation) | = 4.6502 " |
| 7. " " " " (before evacuation) | = 5.3054 " |
| (7)-(6) = Total loss of weight | = 0.6552 " |
| Wt. of air in free space | = 0.0097 " |
| 8. Loss of wt. of charcoal | = 0.6455 " |
| (5)-(8) = Evacuated wt. of charcoal | = 2.0873 " |

A record was kept of every evacuation regarding the loss of weight of the charcoal, in case this data should be necessary in the course of the investigation.

(c) Sorption apparatus: Shewn in Fig. 2A the apparatus consists of a reservoir R (1000 cc) connected by way of T_3 and T_6 to SP, containing a supply of water. Connexion is made to a mercury manometer M, through T_4 , and to the container S by way of T_2 , and ground-joint GS.

Connexion to the vacuum pumps is by way of

- (1) T_1 and T_5
- (2) T_5 and T_6
- (3) T_4 and T_6

Taps T_1 - T_8 are mercury sealed, the remainder are ordinary one-way vacuum taps. The whole apparatus is immersed in a thermostat, water covering the essential parts, the level is indicated by the dotted lines. The thermostat is electrically heated and maintained at $25^\circ\text{C} \pm 0.05$. The apparatus is made in one piece, excepting the container fitting, which is secured by a ground joint covered with Everett's wax and protected by insulating tape.

In all vacuum work, leaks are the chief source of error, and much unexplainable work has been too readily explained away on the grounds of leaks; at least, this is the case in the sorption of vapours by charcoal. To meet this criticism it can be said at once that in this series of work great care has been taken to reduce leakage to a minimum, by careful examination of all taps from time to time, and by testing the apparatus at very frequent intervals. Our experience has been that this apparatus can be maintained at a pressure of the order of 1×10^{-3} mm for very considerable periods, while a vacuum of 1×10^{-4} mm. can be easily held for 48 hours. As all the runs were completed in less than 24 hours the latter figure only concerns the experiments. Before commencing an experiment the water container SP is cut from the apparatus and partially filled with conductivity water. To free the water from dissolved gases, as far as possible, the upper bulb is inverted in hot water, and connexion made to a double-cylinder Geryk oil pump. Pumping is continued in stages with rests in between until the water ceases to boil, except in infrequent bursts, after this the apparatus is re-fused together.

(d) Procedure during a run: The container, with its charge of evacuated charcoal, is connected to ground cup, GS, in the manner already described and the whole apparatus exhausted to less than 1×10^{-6} mm. The water level having been adjusted, all taps are closed and a small amount of water let into the tubing below T_2 . After a short time connexion is made to an evacuated McLeod gauge, via T_7 and T_6 , in order to see if any non-condensable gases have escaped from the water. With careful manipulation fairly approximate figures can be obtained for the presence of any permanent gases. Usually a small pressure is observed, and the pumps are put on to this line for a short time. T_6 and T_7 are then closed and a small pressure of vapour admitted to R via T_3 .

Connexion is made to the charcoal by way of T_3 and the container tap. The fall in pressure is observed by taking frequent readings of the mercury levels in M by means of a cathetometer reading to 0.01 mm. and correct to 0.02 mm. This procedure is repeated until the desired pressure is reached. Equilibrium is judged when the change in pressure is not greater than 0.02 mm. per hour. At this point the container is detached and weighed. Repetition of the above procedure, admitting higher pressures of water vapour, finally brings the charcoal into contact with saturated vapour. To determine the desorption curve the charcoal is opened to decreasing vapour pressures.

4. Apparatus for collection and analysis of evolved water and gases

At the outset of this investigation it was seen that a knowledge of the water and gases given off during the evacuation of charcoal and later of the

recovery of the very strongly held water after experiments had been completed, might be of some use.

Fig. 3A shews the apparatus used. P_1 is a Toepler pump (500 cc. capacity), modified to act as a McLeod gauge. To the left of this pump is a glass vessel *a* (*vide* Fig. 3B), containing phosphorus pentoxide, connected to the leads by means of two ground joints gs_1 and gs_2 . On the right of P_1 is a smaller Toepler P_2 which is connected to a small vessel *b* (*vide* Fig. 3C). Connexion is made,

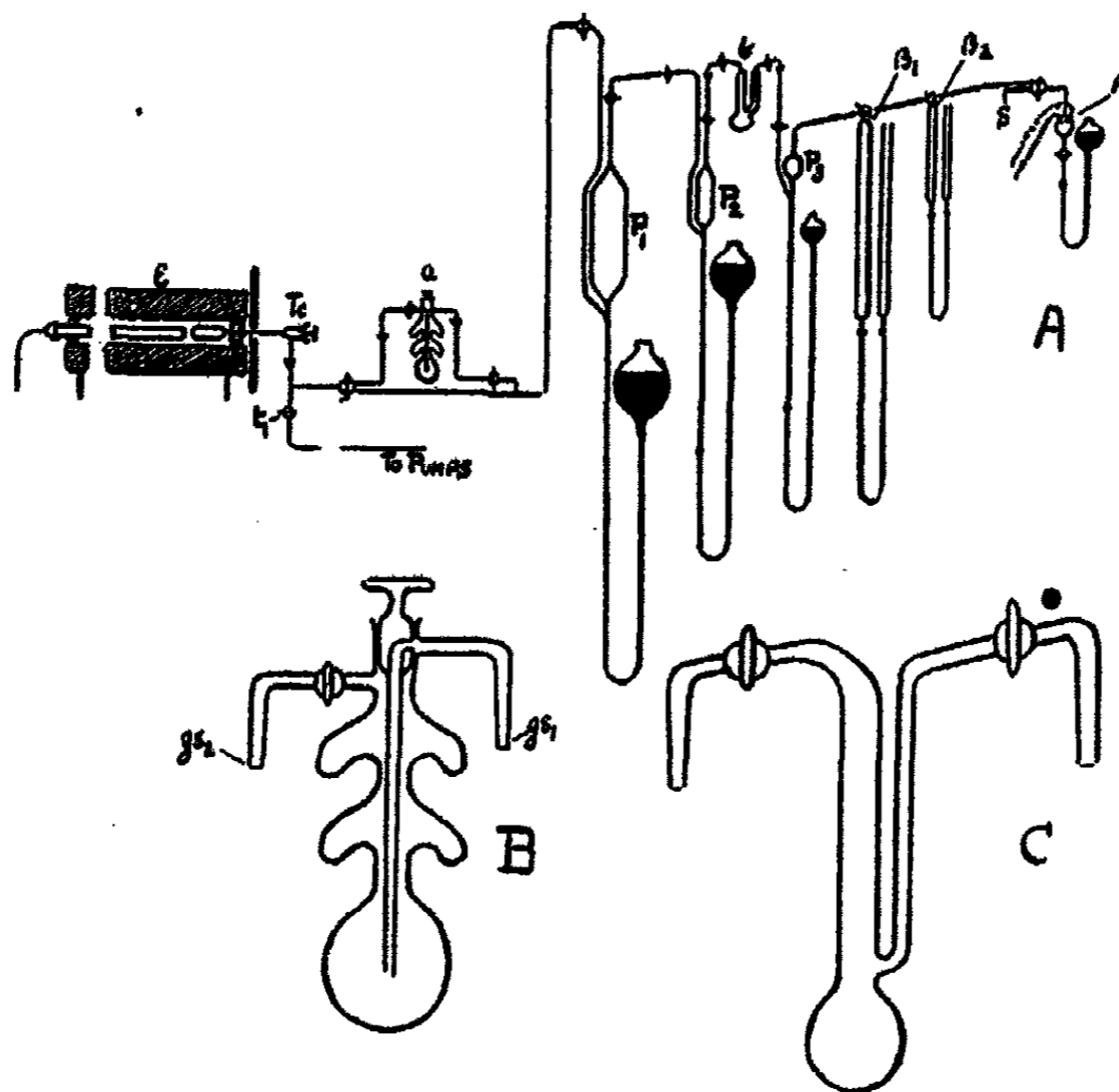


FIG. 3

by way of a third Toepler P_3 , to the gas analysis apparatus consisting of burettes B_1 and B_2 , the former having a capacity of 75 cc. and graduated in 0.1 cc., the latter 10 cc. in 0.05 cc. *A* is a combined absorption and explosion bulb¹ which is connected to the burettes by a two-way capillary tap. The phosphorus pentoxide tube Fig. 3B is so arranged as to present three surfaces of oxide to the incoming vapour. The vessel (Fig. 3C) called a "freezer" is inserted in the line by means of waxed ground joints, in cases where large quantities of water vapour are to be recovered. During an experiment this is surrounded by a mixture of ether and solid CO_2 contained in a Dewar vessel.

To carry out an experiment the phosphorus pentoxide tube is filled with about 3 gms of oxide, evacuated and weighed against a counterpoise. The

¹ Low: *J. Soc. Chem. Ind.*, 41, 1 (1922).

"freezer" is also evacuated and weighed in the same manner. These are then inserted into their respective positions and secured by means of Everett's wax. The whole apparatus is evacuated to a low pressure (1×10^{-4} mm), t_1 shut off and the container tap T_0 (static type shown) opened to a . The temperature of the furnace is raised to the required temperature and any water vapour and gases allowed to expand into a . After a lapse of $\frac{1}{2}$ hour or so the gases are pumped off the charcoal and transferred to the gas analysis apparatus and analyzed, using the usual absorbents in A. Admission of the absorbing liquid being made by way of S.

5. The Charcoals employed

(a) Nature and condition of Charcoals: Three types of charcoals were used. (A) Air-activated birchwood charcoal of British origin which had been carbonized at 900°C and air-activated for 18 hours at $900^\circ\text{--}1050^\circ\text{C}$. (B) Zinc chloride-activated pine wood charcoal of German origin, the conditions of activation not being exactly known but believed to be prepared by treatment with ZnCl_2 , dried at $150^\circ\text{--}250^\circ\text{C}$, and carbonized at 800°C , washed and dried in vacuo at $70^\circ\text{--}80^\circ\text{C}$. (C) Steam-activated coconut charcoal of American origin, activated by the well-known Dorsey process. All charcoals, before use, were graded by sieving through a 10-mesh sieve on to a 12-mesh sieve. The charcoal retained by the latter sieve being used for the experiments.

(b) Analysis of charcoals: The question of the inorganic constituents of charcoal, and its effect on the sorption process being a somewhat debatable question, when this work was commenced it was decided to analyse the charcoals used. The following results were obtained. They are expressed as percentages of the dried charcoal (dried at $140^\circ\text{--}150^\circ\text{C}$ to constant weight).

| | British | American | German |
|--------------------------------|---------|----------|--------|
| Silica an insoluble material | 1.22 | 1.03 | 0.55 |
| Zn expressed as ZnO | | | 1.43 |
| Al " " Al_2O_3 | 0.47 | 0.26 | 0.12 |
| Fe " " FeO | 0.34 | 0.06 | 0.89 |
| Mn " " MnO | 0.07 | 0.007 | 0.016 |
| Ca " " CaO | 1.097 | 0.245 | 0.22 |
| M " " MgO | 0.207 | 0.087 | 0.02 |
| Na " " Na_2O | 0.257 | 0.195 | 0.07 |
| K " " K_2O | 0.30 | 0.90 | 0.726 |
| Alkalinity " " CO_2 | 0.02 | 0.40 | |
| SO_3 " " | 0.197 | 0.057 | 0.503 |
| S | 0.104 | 0.026 | 0.081 |
| Cl " " | 0.207 | 0.093 | 0.422 |
| P_2O_5 " " | 0.134 | 0.075 | 0.029 |

The ash content of each charcoal was determined in the usual manner using a gas-fired muffle furnace. Expressed as percentages of the dried material the results are as follows:

| British | American | German |
|---------|----------|--------|
| 4.59 | 2.20 | 3.90 |

During the evacuation of the charcoals it was believed that a small amount of material, which we termed "sublimate" was laid down on the cold portions of the silica containers. In the case of the British and American charcoals this "sublimate" made its appearance when the charcoals were heated to 800°C and consisted of a narrow band of material, which by reflected light was very similar in appearance to the well-known arsenic mirror deposits. In the case of the German charcoal a small amount of "sublimate" was formed at 270°C and a large quantity at 800°C. This was grayish in colour and formed in wider bands than in the case of the other charcoals. We thought it of sufficient interest to analyse these "sublimates." To do this a special silica container was employed holding about 5-6 gms. of charcoal. To obtain this sublimate the charcoals were outgassed for a considerable period at 800°C until we were certain that no more volatile condensable matter was being evolved. The results of the analysis of the sublimates are as follows (expressed as percentages of the dried charcoals).

| | British | American | German |
|-----------------|---------|----------|--------|
| Free Na | 0.003 | 0.003 | |
| Combined Na | 0.13 | 0.05 | 0.27 |
| " K | 0.10 | 0.05 | 0.28 |
| Cl | 0.24 | 0.09 | 0.49 |
| SO ₄ | 0.20 | 0.01 | 0.006 |
| Zn | | | 0.725 |
| Mn | | | 0.05 |
| Fe | | | 0.03 |

(c) Extraction of charcoals with acid and alkali: In order to investigate the effect of the reduction of the inorganic constituents of the charcoals, two methods of extraction were used.

(1) Acid extraction: In this method batches of charcoal were boiled with concentrated hydrochloric acid for 8-9 hours, renewing the acid lost by evaporation from time to time. The acid was then decanted off and the charcoal transferred to a special glass percolator, where distilled water at about 90°C was allowed to flow through the charcoal until the wash liquid no longer gave a turbidity when tested with 10% silver nitrate solution. The ash content of the charcoals so treated was as follows.

| British | American | German |
|---------|----------|--------|
| 0.31 | 1.34 | 0.12 |

(2) Alkali extraction: Two methods were used, one in which the charcoals were extracted by heating with concentrated caustic soda at atmospheric pressure, the other in which the extraction was carried out under pressure in an autoclave.

Extraction at atmosphere pressure. 100 gms of charcoal was treated with a solution of caustic soda containing 100 gms NaOH. The whole was digested for 7 hours, taking almost to dryness several times. The charcoal was then washed as free from NaOH as possible, digested with concentrated hydrochloric acid for 6 hours, and then washed until the wash liquid gave no reaction with silver nitrate solution. The above process was repeated and the charcoal finally dried at 150°C to constant weight. After this treatment the charcoals gave the following ash figures.

| British | American | German |
|---------|----------|--------|
| 0.295 | 0.125 | 0.14 |

In the case of the American extracted charcoal, a further attempt was made to reduce the ash content by digesting with hydrofluoric acid. The resulting material gave an ash content of 0.10%. In the case of the British charcoal a quantity of ash was prepared and examined both chemically and microscopically. By the latter method it was generally agreed that the substance was almost wholly aluminum silicate. Analysis revealed positive tests for aluminum and silica.

Extraction under pressure. These experiments were unsuccessful as it was found very difficult to free the charcoal from alkali after the extraction had been carried out, presumably owing to the innermost pores of the material having been filled with the solution.

(d) Microscopic and X-ray Examination of Charcoals: Sections of the charcoal were prepared and microphotographs at 100-150 diameters magnification obtained. The results did not hold out much promise of giving very useful information, so the preparation of sections for examination at higher magnifications was not proceed with. Two papers¹ have appeared in which the subject of the microstructure of activated charcoals has been, to some extent, dealt with.

With regard to X-ray work, the charcoals were examined by both the photographic and ionization methods. The results are quite inconclusive, beyond shewing that these activated charcoals are composed of a mixture of graphite crystals and irregularly arranged carbon atoms.

(e) Density of Charcoals: Using a "static" container the charcoal was weighed out in the usual manner and outgassed at either 270°C or 800°C. After cooling and weighing, the L piece of the container was filled with distilled water (25°C) and dipped under the surface of distilled water. The water was admitted to the charcoal by carefully opening the container tap, which was closed after complete entry of water had been effected. The container was then weighed, after removal of all external water. Knowing the volume of container, its weight and also the weight of the container + charcoal, and the weight of the container + charcoal + water, the volume of the charcoal was obtained and hence its density. No claim is made for these de-

¹ Harkins and Ewing: J. Am. Chem. Soc., 43, 1787 (1921); Lamb, Wilson and Chaney: J. Ind. Eng. Chem., 11, 420 (1919).

terminations to represent the true density as "drift" was not allowed to complete itself. The figure for the volume of charcoal will be somewhere between the apparent bulk volume and the true volume.

The results obtained are as follows:—

| | Evacuation temperature | Density |
|---------------------------------|------------------------|---------|
| British | 270°C | 1.880 |
| | 800°C | 1.715 |
| American | 270°C | 1.797 |
| | 800°C | 1.636 |
| American Extracted (NaOH & HCl) | 800°C | 1.618 |
| German | 270°C | 1.678 |

6. Summary

In the foregoing paper the following have been described:

- (1) Apparatus for carrying out sorption and desorption of water vapour by charcoal by both a "static" and dynamic method.
- (2) Apparatus for the recovery, from charcoal, of the sorbed water vapour and gases.
- (3) The results of the analysis of the inorganic constituents of three well-known charcoals, including examination of "sublimates" formed during out-gassing.
- (4) Reference to microscopic and X-ray examination of these charcoals, together with details of extraction of the charcoals by both acid and alkali.

In conclusion it remains for the authors to express their appreciation of the assistance rendered by Professor Allmand, during this work, and to thank those colleagues who assisted in this work.

*King's College,
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November 7, 1927.*

CATALYTIC ACTIVITY OF THALLIUM

BY O. W. BROWN, CHESTER BROTHERS AND G. ETZEL

Introduction

Thallium is an active hydrogenation catalyst¹ and it is one of the three that give high yields of azobenzene. The activity of thallium decreases very rapidly with use. This decrease is probably caused by the melting and running together of the catalyst.

Some catalysts, such as lead and bismuth, may be used at temperatures considerably above their melting points without undergoing any appreciable change in their physical condition. In the case of lead, however, it was found that some lead catalysts ran together while others did not, depending, to a certain extent, upon the physical properties of the oxides from which the catalysts were made. In view of the above, it was thought that a solid support might be found for a thallium catalyst that would adsorb the catalyst without reducing its activity, and thereby prevent it sintering. If sintering was prevented, the useful life of the catalyst would be prolonged.

Experimental Work and Results

The apparatus, method of work, as well as the purification of thallium, were the same as those previously described.² In this investigation, however, the catalyst tube used was a one-half inch diameter glass combustion tube. Three catalysts were prepared from precipitated thallic hydroxide; one was ignited in an electric muffle for two hours at 500°C., and the other at 300°C., while another portion was not ignited. All three were reduced at 230°C. for 3 hours, with the rate of flow of hydrogen of 2 liters per hour. As may be seen in the work referred to above, the temperature at the point where reduction takes place was much higher than at any other part of the catalyst column. In order to keep the temperature as uniform as possible throughout the furnace, the flow of hydrogen was kept low. In spite of this precaution, the catalyst, after reduction, was found to contain globules of massive thallium, showing that it had partially melted and run together. Thus, it may be concluded that an ignited thallium oxide will not give a catalyst which will not melt. In an effort to find a catalyst which could be used satisfactorily without running together, solid supports for thallium were tried. The first of these was aluminum hydroxide, mixed with about 12.8% of metallic thallium. This mixture was prepared as follows: sulfates of thallium and aluminum were mixed and precipitated with ammonium hydroxide. The precipitated hydroxides were thoroughly washed by decantation, filtered, dried, and ground in a mortar to a fine powder. About 25 g. of this powder, which had a light brown color was used to make a catalyst. It was reduced for 3 hours at 230°C., the

¹ Henke and Brown: *J. Phys. Chem.*, 26, 631 (1922).

² Henke and Brown: *J. Phys. Chem.*, 26, 631 (1922).

rate of flow of hydrogen being 2 liters per hr. The catalyst was then used at 245°C. with a resulting yield of 1.7% aniline. At 300°C. the yield of aniline was 5.5%, and at 400°C. was 14.9%. At 400°C. there was also a trace of azobenzene produced. As is evident from the data given, this catalyst was very inactive. However, it appeared to be in good physical condition; it was black and without lustre.

The solid supports next tried were pumice and Nonpareil brick, which were crushed and passed through a 10-mesh sieve, and remained on a 20-mesh sieve. In each case the support was cleaned by boiling in nitric acid, washed with distilled water, and then ignited at 500°C. Each of these were immersed in a thallic sulfate solution, placed in a vacuum desiccator, and evacuated 7 times. The purpose of this was to replace the air in the pores of the support by the thallic sulfate solution. The supernatant thallic sulfate was then poured off and ammonium hydroxide added to the support, which was soaked full of thallic sulfate solution. This precipitated thallic hydroxide in the pores and on the surface of the supports. Each impregnated support was then filtered, washed, and allowed to dry at room temperature.

Thallium on pumice catalyst was used in six experiments at temperatures ranging from 230°C. to 300°C. The rate of nitrobenzene was 4 g. per hr. and of hydrogen 7 liters per hr. No appreciable amount of azobenzene was secured in any experiment. The highest aniline yield was 6.25% at 300°C. This indicates that thallium on pumice is a poor catalyst.

Thallium on Nonpareil brick was used at 245, 260 and 275°C. with the rate of flow of hydrogen at 7 liters per hr. and the rate of flow of nitrobenzene at 4 g. per hr. No appreciable amount of azobenzene was secured. The aniline yield was 6.6% at 275°C., which was the highest yield secured.

Asbestos was the last of the solid supports tried. It was boiled with nitric acid, washed, dried, soaked in thallic sulfate solution, desiccated, and treated with ammonium hydroxide. The catalyst prepared consisted of 24 g. of thal-

TABLE I
Catalyst—Thallium on asbestos
Rate of flow of nitrobenzene—4g. per hr.

| Temperature degrees C. | Flow of hydrogen in liters per hr. | Excess of hydrogen based on azobenzene in per cent of theory | Material yield in per cent of theory | | |
|---------------------------|---------------------------------------|-----------------------------------------------------------------------|-----------------------------------------|------------|-------|
| | | | Aniline | Azobenzene | Total |
| 230 | 7 | 360 | 9.6 | 15.2 | 24.8 |
| 245 | 7 | 360 | 10.7 | 70.9 | 81.6 |
| 260 | 7 | 360 | 16. | 83.7 | 99.7 |
| 260 | 14 | 820 | 12.6 | 83.9 | 96.5 |
| 260 | 7 | 360 | 14.1 | 79.0 | 93.1 |
| 245 | 7 | 360 | 8.4 | 78.2 | 86.6 |
| 245 | 14 | 820 | 4.3 | 81.2 | 85.4 |
| 260 | 14 | 820 | 9.5 | 82.0 | 91.5 |
| 260 | 14 | 820 | 11.8 | 75.5 | 87.3 |
| 260 | 14 | 820 | 7.8 | 74.8 | 82.6 |

lium on 9 g. of asbestos. In order to determine the best working conditions experiments were made at different temperatures and at different rates of flow of hydrogen. The results of these experiments are given in Table I. The yields given are averages of from 2 to 12 experiments.

From Table I it can be seen that the best yields of azobenzene and aniline were obtained at 260°C. The rate of flow of hydrogen which gave the highest yield was 14 liters per hour for azobenzene, and 7 liters per hour for aniline. It may be concluded, therefore, that the best yields of azobenzene are obtained at a temperature of 260°C., and with a rate of flow of hydrogen 14 liters per hour. The activity of the catalyst decreased slightly at first, but after 56 runs it became constant. When temperatures as high as 275 to 280°C. were used the yields of azobenzene were 77 to 75%.

Experiments were also made in this laboratory by Dr. C. O. Henke and E. D. Scudder using a 1½ inch vertical tube iron furnace 12 inches long. The catalyst used contained 60% Tl_2O_3 . The yields obtained were from 85 to 90% theory azobenzene. The production of azobenzene amounted to more than 150 times the weight of thallium in the catalyst before rejuvenation was necessary.

All catalysts tried on solid supports were in good physical condition after being used. The adsorption of thallium by the support was efficient in preventing it from melting and running together, although in the case of aluminum, pumice and Nonpareil brick their presence have reduced the adsorption of hydrogen and nitrobenzene to such an extent as to produce very poor catalysts. Asbestos not only adsorbs thallium preventing its running together, but also does not interfere with the adsorption by thallium of hydrogen and nitrobenzene, resulting in good yields of azobenzene and long life of the catalyst.

Summary

1. Finely divided metallic thallium melts and runs together when used as a catalyst, resulting in a loss of its activity.
2. Thallium on asbestos is an excellent catalyst for the production of azobenzene, and the catalyst retains its activity for a comparatively long period of time.
3. A temperature of about 260° C. gives the highest yields of azobenzene.

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A COMBINED CAPILLARIMETER-VISCOMETER

BY S. THOMAS BOWDEN

13-64

The practical determination of the physical constants of organic and also inorganic liquids has been accorded a considerable amount of attention of late, in view of several recent theories which aim at satisfactory and comprehensive correlation of physical properties with chemical constitution. Similar remarks apply to recent studies of solutions, and in this connexion, it is evident that a systematic extension of our knowledge of the physical properties of solutions is necessary in order to effect a reconciliation between the several existing theories. Among these properties, those of surface tension and viscosity have been brought into especial prominence both in the case of pure liquids and solutions.

In general, the determination of the surface tension and viscosity of a liquid involves the use of separate apparatus in each case. As a result of work proceeding in this laboratory an apparatus has been designed by means of which the determination of the density, surface tension and viscosity may be carried out conveniently and rigidly.

It has been shown by Richards and Combs¹ and Richards and Carver² that the capillary-rise method for the determination of surface tension is entirely reliable when adequate experimental precautions are observed. Accordingly, the present apparatus embodies the principle developed in the Richards capillarimeter, and is of such dimensions that an experimentally plane surface of reference is realized. For the measurement of the viscosity the relative viscometer principle is utilized, and the arrangement is an adaptation of the well-known Ostwald viscometer.

Description of Apparatus.—A diagram of the apparatus is shown in Fig. 1 (a). *A* is a wide tube 5.5 cm. long and 3.8 cm. in diameter, to the lower end of which is fused a bulb, *B*, upon which is etched a mark, *m*₁. Ordinary quill tubing, 4 mm. in diameter, connects the wide tube, *A*, to the capillary tube, *C*, in such a way that the lower end of the capillary tube is above the etched mark, *m*₁, on the bulb, *B*. The capillary tube is carefully selected for uniformity of bore as measured by the usual mercury thread method. In the present apparatus the internal diameter of the capillary tube is approximately 0.5 mm. It is 7 cm. in length, and is arranged parallel to the longitudinal axis of the wider tube, *A*. The upper end of the capillary tube joins to a spherical bulb, diameter 1.5 cm., provided with etched marks *m*₂, *m*₃ above and below. On the other limb, *E*, immediately opposite the lower mark, *m*₃, of the bulb, *D*, is a constriction upon which is etched a mark, *m*₄. The upper part of the tube, *E*, is closed by a well-ground three-way hollow stopcock, *S*, open at the bottom, a cross-sectional view of which is shown in Fig. 1 (b). In the first

¹ J. Am. Chem. Soc., 37, 1656 (1915).

² J. Am. Chem. Soc., 43, 827 (1921).

position, shown in Fig. 1 (a) and Fig. 1 (b), the stopcock provides communication (via the tube, *H*) between the tubes, *G* and *F*, as well as between both limbs of the apparatus. By turning the stopcock through 90° in an anti-clockwise direction, the two limbs of the apparatus are in communication, via the tube, *H*, with *G* only. On the other hand, if the stopcock is turned

through 90° in a clockwise direction from the position shown in the diagram, communication between *F* and *G* can only be effected through the system *EAB-CD*. The stopcock is lubricated with the liquid under investigation.

The short tubes, *F* and *G* possess tapering ends, equipped with well-ground glass caps, whilst the tube, *H*, 1.6 cm. in length, joins the limb *EAB* to *CD*. The over-all length of the apparatus is about 15 cm.

When only a small amount of liquid is available for the determinations, the working volume of the apparatus may be reduced by the introduction of a hollow glass sinker of the form shown in the diagram. This may be conveniently weighted by means of mercury. The underside of the sinker, *W*, is provided with three short projections in order to ensure a free passage of gas through the apparatus during the viscosity determination. Furthermore, in the measurement of the surface tension, it is desirable to arrange the plane reference surface of the liquid approximately half-way in the wide tube, *A*, and, accordingly, the height of the sinker should not exceed this distance.

When the quantity of available liquid is very small, it is advisable to determine the density in a separate pycnometer. In these circumstances, 10 cc. of liquid suffices for the determination of the surface tension and viscosity.

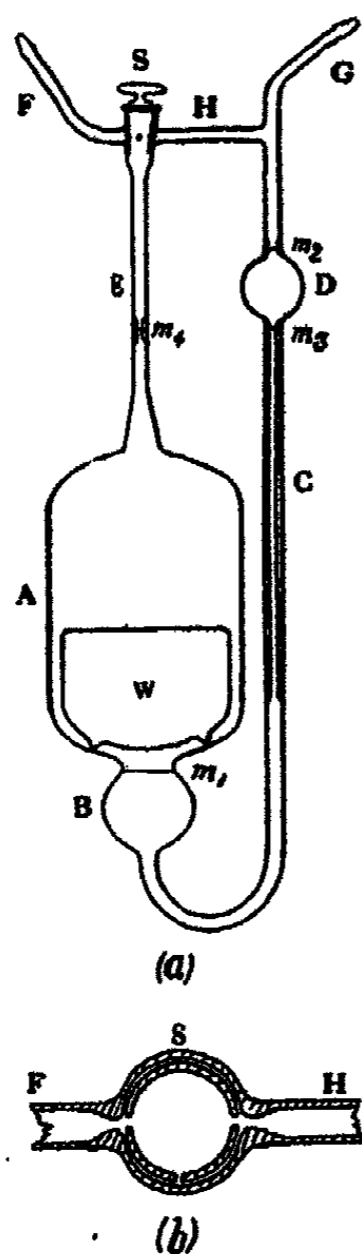


FIG. 1

As is customary in surface tension measurements, the capillary tube is calibrated by means of a mercury thread, the length of which is measured along the capillary by means of a travelling microscope.

Manipulation of Apparatus.—It has been shown by Harkins and Brown¹ that steaming out the capillary tube before a determination brings about a slightly higher capillary rise. With organic liquids, however, the difference is found to be extremely slight. Accordingly, a thorough cleaning of the apparatus by means of warm chromic acid solution followed by rigorous washing with water and a final drying in a current of pure dry air is the procedure which we adopt at present.

¹ J. Am. Chem. Soc., 41, 499 (1919).

The liquid under investigation is introduced into the apparatus through *G* by applying gentle suction at *F*, the stopcock being arranged for communication of the limbs *GDC* and *AEF*. Sufficient liquid is introduced to fill both limbs up to the etched marks, *m*₃, *m*₄. The apparatus is immersed in a carefully regulated thermostat, and the level of the liquid adjusted for coincidence with the etched marks by means of a fine capillary tube. The apparatus is then removed, dried and weighed. A preliminary determination with water or any other standard liquid affords the necessary data for the calculation of the density.

A portion of the liquid is next removed through the tube, *G*, so that the liquid surface occupies a roughly central position in the wide tube, *A*. The apparatus is then set vertically in a thermostat provided with glass sides. After ensuring complete wetting of the tube in the neighbourhood of the meniscus, the capillary rise is measured in the usual manner by means of a cathetometer. In the present apparatus, since the capillary employed is small, the corrected height, *h*, according to the equation of Hagen and Desains,¹ becomes

$$h = h_1 + \frac{h_m}{3} = h_1 + \frac{r}{3} \text{ (when } r \text{ is small)}$$

where *h*₁ is the observed height, and *h*_m is the height of the capillary meniscus. In this manner, the application of the usual formula enables us to calculate the value of the surface tension.

For the purpose of the viscosity determination, a further quantity of the liquid is removed through the tube, *G*, until the liquid surface reaches the etched mark, *m*₁, on the bulb, *B*. The apparatus is arranged vertically in the thermostat, and liquid drawn up to fill the upper bulb, *B*, by applying gentle suction at the end of the tube, *G*. The ground caps are quickly replaced and the stopcock set for communication of the two limbs via the tube, *H*. The time of flow of the liquid between the etched marks, *m*₂ and *m*₃, is observed by means of a stop-watch. The water constant of the apparatus is known from a preliminary determination, and the relative viscosity may be calculated by the usual methods. In this connexion, however, it is advisable, in order to ensure greatest accuracy, to redetermine the water constant of the apparatus from time to time. Owing to inherent errors in the Ostwald type of apparatus, it follows that the degree of precision attainable is considerably below that realized in the measurement of surface tension.

It will be evident that the present apparatus lends itself to the determination of surface tension and viscosity under a variety of conditions. In the case of hygroscopic substances, measurements may be carried out in an atmosphere of dry air, the gas being passed very slowly through the tube, *G*, with the stopcock arranged for communication between *H* and *F*. Incidentally, the apparatus is well adapted for carrying out measurements on reactive substances, such as free radical solutions, dry nitrogen being employed as inert

¹ Ann. Chim. Phys., (3) 51, 417 (1857).

atmosphere in these cases. The combined form of apparatus possesses the further advantage that the measurements are made conveniently and rapidly on the same sample, and that the total volume of liquid required for the determination of the three quantities, density, surface tension, and viscosity, is considerably less than that necessary when the same constants are determined in separate apparatus.

*University College,
Cardiff,
November 16, 1927.*

19-35

NITROGEN-OXYGEN-NITROGEN OXIDE EQUILIBRIA

BY NORMAN W. KRASE*

The investigation into the chemical equilibrium involving the formation of nitric oxide from its elements at high temperatures is a problem that interests both scientific and technical workers. As an example of a pure thermal equilibrium it has been used in the study of rates of reaction and the change of equilibrium with the temperature. Its technical interest arises from the fact that it is one of the oldest processes for the fixation of atmospheric nitrogen. In point of time perhaps it is one of the oldest chemical reactions which still retain modern industrial significance.

The present article is a by-product of an investigation into novel methods of nitrogen fixation.¹ This investigation was based entirely upon published results and involves merely the use of simple physical chemical and thermodynamic principles in arriving at data applicable in new reactions. Since the formation of nitrogen oxides is concerned in one prominent fixation process and in the oxidation of ammonia it is of importance to explore thoroughly the accuracy of the methods on which the principle data are based. Up to the present time the data of Nernst² on the nitric oxide equilibrium have been regarded as classic. The data were obtained by Nernst and his coworkers by heating air to high temperatures, suddenly cooling the gas, and analyzing for nitric oxide by absorbing the products in sulfuric acid. The data so obtained have served as a basis for most calculations involving dependent equilibria. It is significant that the present arc process for the fixation of nitrogen used in Norway appears to substantiate the results of Nernst in regard to yields. In the book of Lewis and Randall³ the various equilibria involving nitrogen and oxygen have been thoroughly analyzed and summarized. The foundation of all the calculations is the data of Nernst and on these data have been erected a large body of related results. For example a very important conclusion, the free energy of formation of nitric oxide from its elements, has been derived. This equation is the following:

$$\Delta F^{\circ} = 21600 - 2.50T$$

A casual inspection of the book will make it evident that the accuracy and dependability of perhaps a dozen calculations are involved in the accuracy of this equation.

Very recently an article has appeared in a French journal⁴ entitled "On the Formation of the Oxide of Nitrogen at High Temperatures," by Briner,

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¹ Published by permission of the editor of the A. C. S. Technologic Series of Monographs. This material is part of the forthcoming monograph on "Nitrogen Fixation" by H. A. Curtis and N. W. Krase.

² Z. anorg. Chem., 49, 213 (1906).

³ "Thermodynamics."

⁴ J. Chim. phys., 23, 788-807 (1926).

Boner, and Rothen. These investigators have reopened the apparently closed question of the nitric oxide equilibrium and have published new experimental results. They point out that the old results of Nernst are subject to at least two errors. First of all, because of the speed of reaction it is entirely probable that the nitrogen oxide formed at a high temperature will decompose very rapidly on leaving the heated zone. They state that this effect is considerable under the conditions used by Nernst. Secondly they point out that the analytical method involved in determining the yield of nitric oxide is unreliable, substantiating that statement by reference to other work in which it is shown that only an incomplete absorption of nitrogen oxides can be obtained by bubbling the gas through sulfuric acid. The equilibrium was re-investigated with improved technique. For example, the gas leaving the heated zone was aspirated very rapidly into a balloon reservoir and left in contact with strong potassium hydroxide for one day. The nitrates and nitrites formed on absorption were then reduced and the ammonia distilled off for titration in dilute acid. In this way the authors claim to be able to determine .002 cc. of nitric oxide. Table I gives the results of the two investigations just briefly described. They were obtained in both cases by heating air to the temperatures indicated.

TABLE I

| T | Per cent NO | |
|------|-------------|--------|
| | Nernst | Briner |
| 1500 | — | .19 |
| 1811 | .37 | .65 |
| 2195 | .97 | 1.86 |
| 2580 | 2.05 | 3.89 |
| 2675 | 2.23 | — |

It is obvious from this table that the new concentrations of Briner are approximately 100% greater than those of Nernst. If we accept the validity of these new results it is of interest to calculate the corresponding free energy of formation and also the effect of the new data on many other important equilibria. This has been done and the new equation based entirely on Briner's data is as follows:

$$\Delta F^{\circ} = 21600 - 3.70T$$

Since it was found that the heat of the reaction as determined by plotting $-\text{Rln}k$ against $1/T$ gave substantially the same value as used by Lewis and Randall in the formulation of their equation, merely a new constant has been calculated.

The free energy of formation of the oxides of nitrogen depends very considerably upon the free energy of formation adopted for nitric oxide. The corresponding thermodynamic quantity for nitric acid likewise depends on the value ascribed to nitric oxide. Table II lists in parallel columns the old free energy values given by Lewis and Randall and the new values calculated on the basis of Briner's data.

TABLE II

| Compound | ΔF_{298}° | |
|-----------------------------------|--------------------------|--------------|
| | Lewis and Randall | Recalculated |
| NO (g) | +20850 | +20500 |
| NO ₂ (g) | +11920 | +11570 |
| N ₂ O ₄ (g) | +22640 | +21900 |
| HNO ₃ (g) | -18210 | -18560 |

It is seen that the change involved is of the order of 2 to 3%. This in many cases makes a very large difference in the concentrations obtainable at equilibrium.

Summary

The free energy of formation of nitric oxide from its elements has been recalculated on the basis of the latest published data. A new equation expressing the relation between the free energy of formation and the temperature has been developed. The importance of this relationship in many other equilibria has been emphasized.

THE EQUILIBRIUM (POLARIZATION) COMPOSITION OF THE
LIQUID SALT PHASE AND THE LIQUID ALLOY PHASE IN A
SYSTEM COMPOSED OF EQUIATOMIC QUANTITIES
OF SODIUM, POTASSIUM, AND IODINE

BY HERBERT F. SILL

Recent studies by Lorenz, Fraenkel and Silberstein¹ and by Tammann and Bohner² contain data showing the equilibrium distribution of the elementary components in the following two-liquid-phase, three-component systems.

Cadmium-lead-chlorine

Cadmium-thallium-chlorine

Iron-copper-sulphur

In the first of these systems both metallic components are divalent, replacing one another atom for atom. In the second and third systems one is di-valent and the other monovalent. The system here presented constitutes an extension of the list to include a system in which both components are monovalent.

The data for the first two systems extend over a wide range of variation in the atomic proportions of the three elements present and the phase compositions corresponding either to equiatomic or to chemically equivalent proportions can be accurately interpolated. The data for the iron-copper-sulphur system apply only to the case in which the components are present in chemically equivalent proportions, i.e. in the atomic proportion of 1:2:1.

The system sodium-potassium-iodine.

Materials. (a) Sodium and Potassium Iodides. A quantity of c.p. salt (Merck) was in each case fused in a platinum dish and on solidifying was ground and preserved over P_2O_5 .

(b) Sodium metal. Commercial sodium analysing 97.2% Na was distilled in hydrogen, a wide-bottomed Erlenmeyer flask being used as a receiver. A part of the kerosene in which the commercial metal had been preserved was transferred to the receiver and the latter warmed on a hot-plate until the metal melted and formed a shallow layer beneath the kerosene. By gently shaking the metal was caused to separate into large globules which presently solidified. The kerosene was decanted and the globules washed by repeated decanting with Na-dried petroleum ether B.Pt. 75° the final addition of petroleum ether being left in the flask.

(c) Potassium metal. Globules were prepared directly from the laboratory supply without distilling. The procedure was otherwise the same as that employed for the sodium.

¹ Z. anorg. Chem., 131, 247 (1923).

² Z. anorg. Chem., 135, 166 (1924).

The method and numerical result of the analysis of the two metals is given below in connection with the analysis of the equilibrium alloys.

Containers. Pieces of soft steel tubing 15 cm. long and 15 mm. inside and 20 mm. outside diameter were brightly polished within and without and at each end the bore of the tube was slightly enlarged for a distance of one cm. The tube, supported in a clamp, was submerged over four-fifths of its

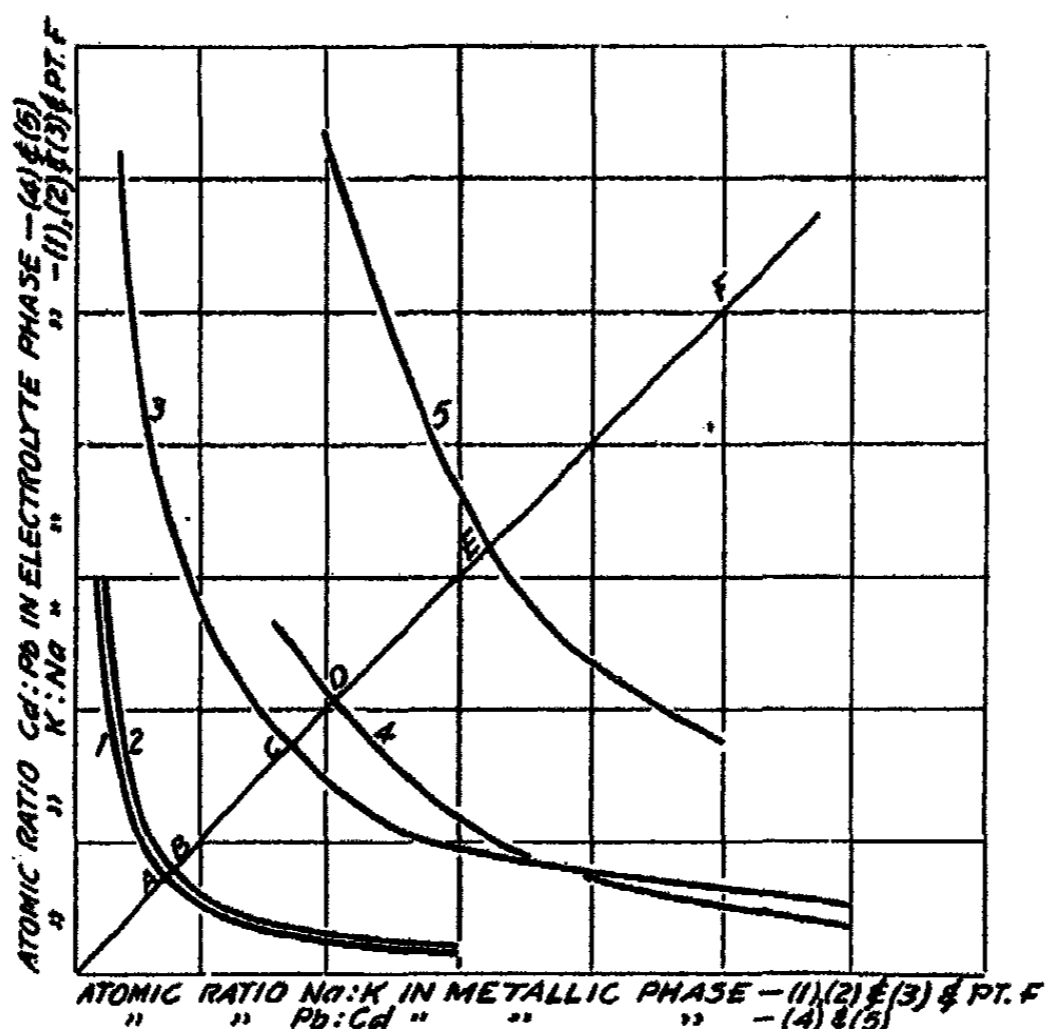


FIG. 1.

length in a pail of water leaving 3 cm. exposed. A tightly fitting steel plug was placed in the upper end and sealed in with an oxy-acetylene torch. On connecting it with a manometer and evacuating the seal was found to be tight.

Charging the tube. Two large sodium globules which had remained bright and untarnished in the petroleum ether were taken up with a forceps, dipped in Na-dried ethyl ether and transferred to a vacuum weighing-tube. The latter was evacuated to remove the ether and the weight of the metal determined. An amount of potassium iodide chemically equivalent to the sodium was weighed out, dried air was admitted to the vacuum-tube and the metal globules transferred to the steel tube followed by the weighed portion of the salt. The mouth of the tube was closed with a steel plug and sealed as before.

Heating. An electric tube-furnace was used for heating the reaction materials. The furnace-tube employed was a 60 cm. length of steel tubing of 3 cm. bore. This tube was inserted horizontally through the furnace opening and attached at one end to a geared motor. The other end was supported in a semicircular bearing cut in piece of graphite plate. An ammeter was

placed in the heating circuit and a thermo-couple inserted axially in the furnace-tube. The tube was then rotated at 70 R.P.M. and the current required to maintain a constant temperature of 700° and 725° respectively was determined.

The thermo-couple was put aside and the furnace-tube taken from the furnace and allowed to cool. The sealed reaction-tube was now placed within the furnace tube and secured in a slanted position by means of a plug of heavy steel turnings rammed in from each end and the whole replaced within the furnace and rotated as before for ten minutes at 725° and for fifty minutes at 700°.

The volume of liquid material within the reaction-tube could be calculated to occupy about half the available space. The effect of the rotation and the gravity movement due to the inclined position of the reaction-tube would be a somewhat spiral flow back and forth with each revolution.

The furnace-tube was disconnected from the motor, and tube and furnace together were turned to a vertical position, the heating current being meanwhile continued. The tube was raised and allowed to drop repeatedly on a steel block placed below, in order to promote the complete coalescence and segregation of the material belonging to each liquid phase. It was then removed from the furnace and allowed to cool.

The reaction-tube was extracted from the furnace-tube and placed upright in a vise. The upper end of the tube was then removed with a pipe-cutter and the tube at once filled with Na-dried kerosene. The bright surface of the solid alloy could be seen below. The alloy was melted by dipping the tube in hot kerosene and the liquid contents of the tube, viz. kerosene and alloy, were decanted into a small flask containing additional hot kerosene. The metal, which coalesced to form a single large globule was allowed to solidify, rinsed successively with petroleum ether and ethyl ether and transferred to the vacuum weighing-tube and the weight obtained.

The weighed globule was transferred to a platinum dish and placed together with a beaker of water under a bell-jar.

The resulting syrupy hydroxide solution was diluted and aliquot portions titrated with $n/5$ HCl. Here the requirements of precision analysis were carefully observed, the volumetric glassware having been standardized by weight and the normality of the acid determined against anhydrous sodium carbonate.

A weighed globule of the distilled sodium-metal used as initial material was treated and analysed in the same manner, the calculation yielding the value 100.05% Na.

The reverse reaction was now carried out in a second reaction-tube charged with chemically equivalent quantities of potassium-metal and sodium iodide, the same conditions as to time, temperature and manipulation being observed throughout.

The titration analysis of the initial potassium-metal gave the value 99.85% K.

For each of the alloy globules the titration gave the sum (s) of the gram-atoms of sodium and potassium therein contained. From this value and its weight in grams (w) the number of gram-atoms of sodium (x) and the number of gram atoms of potassium ($s-x$) are calculated from the equation $23x$ plus $39.1(s-x) = w$.

The experimental data and the derived values are contained in the following table:

| initial reacting substances | weight of alloy (w) | total gram-atoms (s) | gram-atoms sodium (x) | gram-atoms potass. ($s-x$) | atomic ratio Na:K |
|-----------------------------|-------------------------|--------------------------|---------------------------|------------------------------|-------------------|
| Na&KI | .7607 | .03138 | .02896 | .00342 | 11:1 |
| K&NaI | .4456 | .01804 | .01615 | .00189 | 9:1 |

The difference in composition of the two "equilibrium alloys" can not be assigned to analytical error and since the equilibrium was approached from each side under identical conditions of temperature and of rate and duration of mechanical agitation the true value for the equilibrium atomic ratio Na:K in the alloy may be placed half-way between the above values or at 10:1.

The direction of the divergence from the true value is, for the two incomplete reactions, what would be expected. Where sodium constituted the initial reacting metal its preponderance in the alloy is greater than where all the sodium appearing in the alloy had to be derived by displacement from the compound.

Jellinek and Czerwinski¹ and Jellinek and Tomoff² determined the equilibrium ratios Na:K and KCl:NaCl for a system in which a lead solution of the alkali metals and a fused chloride mixture constituted the respective liquid phases. Owing to the relatively "noble" character of the lead the electrolyte phase consisted virtually of the alkali chlorides only. The determinations involved the initial reacting substances in widely varying proportions and were conducted at a temperature of 1000 degrees.

Their results are given in the following table.

| Na:K | KCl:NaCl |
|------|----------|
| 17.0 | .87 |
| 12.5 | 1.04 |
| 5.25 | 2.12 |
| 4.30 | 2.63 |
| 1.50 | 6.94 |
| .725 | 12.35 |

The same relationships had been previously determined by G. M. Smith and T. R. Ball³ for a system in which a dilute solution of the alkali metals in mercury formed the metal phase and a water solution of the chlorides the elec-

¹ Z. physik. Chem., 110, 172 (1924).

² Z. physik. Chem., 111, 234 (1924).

³ J. Am. Chem. Soc., 39, 179 (1917).

trolyte phase. Here likewise the "noble" metallic component was virtually present in the metal phase only.

In the system of Jellinek et. al. the *total* salt concentration in the fused salt mixture comprising the electrolyte phase remained essentially constant throughout the wide range of variation in the salt *ratio* KCl:NaCl.

In the Smith and Ball system, owing to the presence of water as the chief constituent of the electrolyte phase, the total salt concentration could also be widely varied.

In the diagram the point F represents the result of the investigation previously described for a system composed of equiatomic quantities of sodium, potassium and iodine. This system contained no "solvent" water in the electrolyte phase nor "solvent" noble metal in the metallic phase. The curve 3 represents the Jellinek data, i.e. for a system containing "solvent" lead in the metal phase and chlorine instead of iodine in the electrolyte phase. The curves cutting the diagonal at B and A represent respectively Smith and Ball data for systems of 4.0 normal and of 2/10 normal total salt concentration, i.e. for a system containing a diluent in both phases.

The intersection of each curve with the diagonal of the diagram represents the reciprocal relationship Na:K in the metal phase and K:Na in the electrolyte phase when the components sodium, potassium and halogen are present in the system in equiatomic quantity. The curve 5 represents the system cadmium-lead-chlorine and the curve 4 the same active components with the addition of the relatively "noble" (inactive) metallic component antimony. The intersection of each of these two curves with the diagonal gives the atomic ratio Pb:Cd and Cd:Pb when these two components are present in the system in equiatomic quantity.

A comparison of the points F, C and B shows that so far as composition changes are concerned, the combined effect of replacing the iodine by the more electro-negative chlorine and of dissolving the alkali-metal binary alloy in the less electro-positive lead has been to reduce the equilibrium atomic ratio from 10 to 3.4 and that the combined effect of a further substitution of the "solvent" lead by the still less electro-positive (nobler) mercury and the introduction of "solvent" water has been to further reduce the ratio to the value 1.5.

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NEW BOOKS

A Dictionary of Applied Chemistry. Vol. VII. By Sir Edward Thorpe. 22 × 15 cm; pp. viii + 573. New York and London: Longmans, Green and Co., 1927. Price: \$20.00. This is the seventh and last volume of this impressive set. Among the interesting topics in this section of the alphabet are thallium, theine, thermometers, thermostats, thiophen, thorium, thyroid gland, tin, titanium, tobacco, toluene (84 pp.), toxins, triphenylmethane coloring matters, tropeines, tryptophan, tungsten, turpentine, tyrosine, ultramarine, uranium, urea and urine, vanadium, vanillin, varnish, vat dyes, vitamins, water (106 pp.), wax, whiskey, wine, destructive distillation of wood, xylenes, yeast, yttrium, zinc, zirconium.

"The fact that theine (caffeine) exists in the leaves of the coffee plant has long been known, but it is only since the war that they have been commercially exploited to produce this drug. The idea originated in Sumatra, where, under the present system of cultivation, coffee is frequently attacked by insects of the genus *coccus*. With the failure of the berry drop, the growers, seeking a substitute for the ordinary caffeine-containing product, collected the leaves from which pure theine was prepared. With the war the demand for theine so greatly expanded that the process of extracting it from the leaves was resorted to on an extensive scale by the Dutch factories, which purchased them by the ton from the native growers and pickers. So far, the process of preparation has been kept secret, but there is no gainsaying the purity of the product. On the western side of the island of Sumatra the producers, and, in fact, the general public, have long used an infusion of torrefied coffee leaves as a beverage, the berries themselves all being reserved for export. The use of the leaves for this purpose has grown to such an extent that it is now looked upon as an absolute necessary of life.

"During the past four years Germany has been importing enormous quantities of coffee leaves from Sumatra and utilizing them in the same way; and in some parts of Germany the infusion from the leaves has quite taken the place of the berry, the price of which has been an obstacle to its ready sale. Careful research work has resulted in proof that the extract obtained from the leaves has undoubted nutritive properties. In addition, a vast number of analyses have been taken which furnish data practically guaranteeing its safety as an article of diet, with an entire absence of deleterious effects. With a little boiled rice and infusion of the coffee leaf a man will support the labours of the field in rice-planting for days and weeks successively up to the knees in mud, under a burning sun or drenching rains, which he could not do by the use of simple water, or by the aid of spirituous or fermented liquors. Planters in Sumatra had opportunity of observing for twenty years the comparative use of the coffee leaf in one class of natives, and of spirituous liquors in another, the native Sumatrans using the former, and the natives of British India (imported labour) the latter. Records show, while the former expose themselves with impunity for any period to any degree of heat, cold and wet, the latter can endure neither wet nor cold for even a short period without danger to their health. Although the coffee berry can only be produced in certain climates and on soils containing marked peculiarities, the plant itself will flourish in any tropical country where the soil is sufficiently fertile, and in consequence the field for production of the leaves is almost unlimited. As a means, therefore, of providing caffeine for general consumption free from deleterious qualities, and yet containing great nutritive properties, the leaves appear to be eminently suitable," p. 5.

Under thermit process, p. 7, we read that "owing to the heat developed in these reactions and the rapidity with which they occur, an enormous temperature is produced, second only to that of the electric arc. It has been estimated at 2600°-3000°, and direct observation with a Féry radiation pyrometer has shown that the temperature of a stream of steel produced from iron oxide and aluminium, as it was poured from the crucible, was 3200° (the melting point of steel is approximately 1350°). At such temperatures the entire contents of the crucible remain liquid; the reduced metal sinks to the bottom, covered with a layer of molten alumina."

One hundred parts of thoria can hold in solid solution 6-7 parts of cerium dioxide, and as the mantle contains only about one percent of the latter, the ceria is entirely dissolved. "Although in most instances the optimum effect is attained by mixing the thorium and cerium salts in such proportions that the mixed oxides of the mantle consist of 98.8 p. c. of thoria and 1.5 p. c. of ceria, yet owing to the yellow colour of the light produced by this amount of ceria in inverted mantles, it is customary in this form of illumination to reduce the proportion of ceria to from 0.5 to 0.7 p. c.," p. 40.

"Titanox consists of titanium dioxide precipitated upon a base of finely divided *blanc fixe*. In colour it is far whiter than white lead, but not quite so white as French process zinc oxide or the best grades of lithopone. Its hiding power is twice that of white lead and is the greatest of any white pigment. Its inertness towards varnish liquids enables it to be used in compositions that can be kept without danger of livering or thickening. 100 p. c. titanox in oil dries very slowly to a soft film, and a fair quantity of a metallic drier should be used while for interior work an addition of about 30-50 p. c. of zinc oxide is advantageous, this causing it to give a firm dust-resisting film. Titanox appears to be very resistant to sunlight and to all atmospheric conditions and to hydrogen sulphide fumes," p. 72.

"Titanium oxide is used as a mordant, and in at least two cases it has an advantage over alumina; thus alizarin yellow produces with titanium as bright but a much faster colour than with alumina, whilst the scarlet obtained from alizarin orange on a titanium mordant is the fastest scarlet that can be obtained on wool," p. 73.

"The venom of scorpions (against which an antitoxin can be prepared) and spiders is probably protein in nature; of mosquitos and gnats it may be the products of certain bacteria or moulds present in the oesophageal sacs; of bees a protein-free organic base. The formic acid present in the 'venom' of ants, bees, etc, is probably not the active toxin. Many fish are also poisonous by their bites or by spines connected with special glands. Toads and salamanders have acid poisons and basic poisons in the skin glands. Jelly-fish and sea-anemones have stinging glands. Extracts of intestinal worms may be toxic," p. 176.

"With regard to liquid water, there is a great body of evidence pointing to the presence of complex molecules. It is now fairly generally held that the abnormality of water as compared with other liquids in so many physical properties is due to polymerisation. This explanation was first advanced by Whiting [A New Theory of Cohesion applied to the Thermodynamics of Liquids and Solids, Harvard University, Cambridge, Mass., 1884, p. 70], who pointed out that water at 0° may contain 25-38 p. c. and at 100° 17-28 p. c. of dissolved ice, and that the observed expansion of 4 p. c. by volume in this interval is the resultant of a normal expansion of some 8-10 p. c. by volume and a contraction due to the melting of the dissolved ice. Eight years later Röntgen [Wied. Ann., 45, 91 (1892)], independently suggested that water consists of 'ice molecules,' and water molecules the former being more complex but less dense than the latter," p. 361.

"The waxes differ from the fats in having little or no greasiness at ordinary temperatures. The greasiness of most of the fats is probably due to their containing some olein (glyceryl oleate) or some glyceryl esters of unsaturated fatty acids. There was an impression in the last century, doubtless produced by Chevreul's work on the fats, that whilst the fats contained glyceryl esters, the true waxes did not; but contained esters of higher members of the $C_nH_{2n}O_2$ series of acids with alcohol radicles other than glyceryl. As a result of this an unfortunate system was introduced of denying the name of 'wax' to those waxes that are largely composed of glycerides, and of calling them 'tallows.' It serves no useful purpose and has the effect of upsetting the ordinary meaning both of 'wax' and of 'tallow.' By it, on the one hand, Japan wax was to be called Japan tallow and myrtle wax was to be called myrica tallow, because they are both largely composed of glyceryl palmitate; and on the other hand, sperm oil was to be described as a liquid wax, because it was thought to contain very little glyceryl esters. Refined wool fat, a soft unctuous substance, was called wool wax. The inadvisability of attempting to alter the meaning of a word in common use to suit some special scientific classification was pointed out by Gregory in Nature, 87, 538 (1911)," p. 434.

"The generally held view that the browning of wines is due to unsound grapes is not correct. The presence of stalks in the fermenting mash contributes appreciably to browning. Very acid wines are particularly prone to browning. The browning is most probably due to the oxidation of tannin-like substances of phenolic character by the action of oxidases, or by auto-oxidation, or probably by both processes. It can be prevented, at least to a considerable extent, by immediately pressing the grape mash, but this course is not always possible in practice.

"The browning of wines which is not only accompanied by a discoloration, but also with a strong turbidity and an unpleasant flavour, can be arrested by the use of sulphur dioxide in the form of potassium metabisulphite, which is added to the juice in the cask before fermentation. The yeasts can withstand without risk quantities of sulphur dioxide towards which *Bacterium gracile*, which effects the decomposition of malic acid at the close of the fermentation, is sensitive. The inhibition of the decomposition of the acid, whether it be temporary or complete, is mainly dependent on the quantity of free sulphur dioxide,"

P. 474.

"According to A. Dupré, fraudulent colouring matters added to red wines may be detected by dialysis, which is best accomplished by placing in the wine a cube of jelly about $\frac{1}{4}$ inch side. These cubes are made by dissolving 10 grms of gelatin in 100 c. c. of warm water, and pouring the solution into a flat dish or mould; from the plate thus obtained the cubes are cut. After 24-48 hours, the cube, on examination by transmitted light, will be found to be coloured more or less deeply by any colouring matter present, excepting the natural colouring matter, which penetrates only to a depth of $\frac{1}{4}$ inch at the most. The colouring matter of alkanet root also penetrates but slowly, whereas rosaniline, cochineal, logwood, brazil-wood, indigo, litmus, red cabbage, beet-root, *Makva sylvestris*, and *Althea officinalis* penetrate rapidly into jelly," p. 485.

Wilder D. Bancroft

The Microbiology of Cellulose, Hemicelluloses, Pectin, and Gums. By A. C. Thaysen and H. J. Bunker. 22 x 16 cm; pp. viii + 383. London and New York: Oxford University Press, 1927. Price: \$8.50. In the preface the authors say, p. v.: "In order to avoid misunderstanding it should be mentioned perhaps that the term micro-organisms has been adopted to designate all microscopic organisms whether they belong to the animal or to the vegetable kingdom, and that colloquially the word 'bacteria' has been used for all the red-shaped schizomycetes belonging to the subbacteriales. Where a distinction in the Latin nomenclature has been necessary among the bacteria, the system followed by Lehmann and Neumann and by Bergey has been adhered to and a spore-producing rod termed *Bacillus*, a non-spore-forming *Bacterium*."

The subject is presented under four chief headings: cellulose, hemicelluloses, pectin, and gums; the types of microorganisms associated with the decomposition of cellulose, hemicelluloses, pectin, and gums; the microbiological decomposition processes of gums, pectin, hemicelluloses, and cellulose; industrial applications.

"Pectin, which most authors regard as insoluble, is sometimes described as proto-pectin (Tschirch and von Fellenberg), and sometimes as pectinogen (Schryver and Haynes), or pectose (Carré). The proto-pectin is said to become soluble in the cell sap on the ripening of fruits, and it can be rendered soluble by prolonged boiling with water or alcohol or by treatment with dilute acids (Carré), or with salts of acids which form insoluble calcium salts, such as ammonium oxalate, ammonium tartrate, or sodium carbonate (Clayson, Norris, and Schryver). The soluble compound from ripe fruits is termed pectin by von Fellenberg and cytopectic acid by some English investigators. Von Fellenberg's pectin, which is neutral, is claimed to be the methyl ester of pectic acid. It is saponified by treatment with alkali in the cold and thereby yields methyl alcohol, amounting to some 10 per cent. of the total pectin or cytopectic acid," p. 11.

"A third line of research into the natural decomposition of cellulose and its associated substances was initiated in 1875 by Popoff, who investigated the causes of the natural evolution of methane in stagnant ponds. He found that methane is produced from cellulose

and its related substances, such as gums, deposited at the bottom of ponds, and that a methane fermentation could be artificially started if a flask filled with water and substances containing cellulose were inoculated with mud. The methane evolved during the resulting fermentation was sometimes found to be mixed with small amounts of hydrogen," p. 19

"*Bac. fossicularum*, Omelianski's hydrogen-producing cellulose decomposer, is associated with *Bac. methanigenes* wherever the latter occurs, and can therefore be obtained from mud. The rate of germination of its spores is slower than that of the spores of the methane bacillus, and this fact was utilized by Omelianski for the separation of the two. It was mentioned above that the gas evolved by the first crude culture prepared for the isolation of *Bac. methanigenes* contained hydrogen as well as methane. If such a culture is heated to 75° C. for fifteen minutes shortly after the gas evolution has commenced, the vegetative cells of the methane bacillus which have by then developed from their spores are destroyed, whereas the spores of the hydrogen bacillus, not germinated, remain unaffected by the heat. Repeating this treatment through three or four successive generations from the original crude culture, a culture is obtained which gives off a gas containing hydrogen and carbon dioxide only. It is interesting to note that when the methane organism is subjected to the same treatment it is eventually destroyed. This disposes of the possibility that the organism responsible for the evolution of the mixture of methane and hydrogen can be one and the same type, which through subjection to a high temperature loses its property of producing methane, but maintains its faculty of evolving hydrogen. That the two organisms are not the same species is also indicated by their difference in size," p. 57.

"The art of retting plant tissues for the isolation of fibres has been carried out in many countries from time immemorial, and highly developed methods for the retting of flax existed in countries such as Egypt from the earliest dynastic times. Here conditions were undoubtedly particularly favourable, the river Nile with its slow-moving and comparatively warm and soft waters forming an ideal basis for the elaboration of a natural retting process. A different method was probably adopted by the inhabitants of the Swiss lake dwellings, who, it appears from the remains found, were well acquainted with the art of retting. Here the process was probably carried out in stagnant water. Both of these methods, the retting in stagnant and in slow flowing water, were the only two anaerobic retting processes in use up to the middle of the nineteenth century. They are still extensively used, the former in Ireland and Italy, the latter in Holland, Belgium, and Germany," p. 163.

"The ochre pigment formed by many cellulose-decomposing bacteria was examined by Hutchinson and Clayton in their investigations on *Spirochaeta cytophaga*. They found that the pigment is soluble in the ordinary fat solvents, yielding a canary-coloured solution with ether, an ochre-coloured solution with petroleum ether or chloroform, and an orange-coloured solution with carbon bisulphide. On evaporation of these solutions an oily orange-coloured residue remained. The pigment gives color reactions resembling those of carotin. It therefore resembles the lipochrome pigments found in many bacteria, for instance in *Staphylococcus pyogenes aureus*," p. 189.

"Both in the manure heap and in the compost heap the microbiological changes, resulting in the 'ripening' of the heap, aim at the conversion of the vegetable tissues present into compounds which will assist in maintaining and increasing the fertility of the soil. Primarily the heap is converted into the so-called *beurre noir* of the early French investigators, now generally described under the name humic substances. To carry out these changes in the soil itself has long been known to be deleterious to plant life unless sufficient time is allowed to elapse for a fresh state of biological equilibrium to be established. This harmful effect was demonstrated by Fred in the case of green manure. Where seed was sown immediately after ploughing in green plants as a manure, the seeds, or the seedlings germinating from them, were destroyed by fungi, and possibly bacteria, active in the conversion of the green manure. The micro-organisms thus attacked both the tissues which they were intended to destroy, and the other forms of vegetation present within the sphere of their activity. Not until the equilibrium of the soil-flora has been restored, on the complete

destruction of the green manure, can plant life benefit from the resulting decomposition products. In the case of green manure this destruction is usually completed in a few weeks," p. 195.

"The problem of the decomposition of cellulose and hemicellulose under water is at least equal in importance to that of their destruction in the soil. In lakes, marshland, and canals, in tropical climates, in mangrove swamps, and in the sea of all climates, tremendous quantities of vegetable debris composed largely of cellulose or hemicelluloses accumulate and decay, chiefly through microbiological activity. Very little is known of the reactions involved except that marsh gas is frequently formed as a result of the decay. This gas at first remains entangled in the mud of the water bed, but eventually rises to the surface of the water, either as bubbles or sometimes in a continuous stream. It is this gas which, when becoming spontaneously ignited, was known of old as the will-o'-the-wisp," p. 213.

"When hay or other plant material is loosely stacked before it becomes dry, it shows a tendency to heat or sweat, a phenomenon which in extreme cases may result in its spontaneous ignition. As in the case of ensilaging, the reactions involved have been ascribed to microbiological, plant physiological, and chemical agencies; but, in spite of statements to the contrary, available evidence undoubtedly favours the explanation that micro-organisms are responsible for most of the earlier stages of the reactions. Miede, who undertook a comprehensive study of the phenomenon, came to this conclusion, and Haldane and Makgill in a later publication confirm this view after due consideration of the evidence brought forward by Boekhout and de Vries in favour of a chemical explanation, and of Tschirch's suggestions, attributing the heating to the activity of oxydases and reductases secreted by the plant tissues," p. 201.

"Just as the tobacco fermentation shows analogies to the spontaneous combustion of hay, so do the cacao fermentation and perhaps the coffee fermentation resemble the silage fermentation and much light could undoubtedly be thrown on both of these processes if they were considered from that point of view," p. 237.

"Assuming that the decay in the peat bog does proceed under waterlogged and more or less anaerobic conditions, there is every justification for asserting that, in the best of cases, microbiological activity must cease in the peat before the cellulose and the hemicelluloses of the submerged plant material have been approximately eliminated. The complete disintegration of the plant material and the progressive elimination of the cellulose, which Fischer and Schrader have undoubtedly shown to occur, must therefore be performed by other agencies than micro-organisms, which it would be beyond the scope of this volume to discuss.

"Some evidence for this conception of the formation of peat and coal has been brought forward in a recent paper by Thaysen, Bakes, and Bunker. It is suggested in this publication that microbiological activity ceases in the upper layers of the peat bog before the bulk of the cellulose has disappeared, and that the subsequent destruction of the cellulose proceeds on lines similar to those active in the production of carbohydrate humus from linen cloth through ageing. It is shown that the humus compounds of a normal peat bog, after chlorination by the methods recommended by Eller and his collaborators, can be split up into two substances, one identical with the humus compound obtainable from quinones and lignin, and the other with the composition of the artificial humus compound obtainable from sugars and other carbohydrates by the action of acids. The latter type of humus was also obtained by these workers from samples of Egyptian mummy cloth made of pure undyed linen which had decayed in the absence of micro-organisms," p. 248.

"Fungi decaying the heartwood of living trees are not commonly found in wood used for aeroplane structures. Where they do occur, they are effective proof that the wood used was originally infected, and that sufficient care had not been exercised in eradicating the seat of infection. Decay in wooden aeroplane parts has become far more important in recent years, since large numbers of spare parts have often to be stored for a long time. Such parts should, in Boyce's opinion, be kept under conditions which will permit of good ventilation and will ensure that the moisture content of the wood does not exceed 11 per cent.

Aeroplanes in use, quite apart from those employed in very damp tropical climates, are in parts exposed to decay, particularly near the engine and around the base of the wings, where an increased humidity and a somewhat higher temperature prevail," p. 296.

"Though the marsh gas which escapes from the ground in some localities has been used as a combustible gas for domestic purposes for many years, and though numerous investigations have shown that the microbiological decay of vegetable debris frequently gives rise to the evolution of such gases, especially methane and hydrogen, few attempts have so far been made to utilize these reactions for the commercial production of gaseous fuels. Those made have not yet succeeded in establishing this industry, even in localities where vegetable debris is abundant and coal deficient. This no doubt, is largely due to the existing imperfect knowledge of the microbiology of hemicelluloses and cellulose, and to the consequent difficulties encountered in attempting to control the breakdown of these substances on a technical scale. There is no *prima facie* reason to believe that such processes should necessarily be uneconomical. On the contrary, they appear to constitute a fruitful field for future investigations," p. 313.

Wilder D. Bancroft

The Chemistry of Wood. By L. F. Hawley and Louis E. Wise. 23 × 17 cm; pp. 334. New York: Chemical Catalog Company, 1926. Price: \$6.00. In the introduction, p. 15, the authors say: "To the best of our knowledge, no attempt has hitherto been made to bring together within the compass of a single book, data pertaining solely to the chemistry of wood. Our own attempt to develop a monograph on this subject therefore resembles a pioneering adventure. We have worked unhampered by trials or precedents, and if our volume contains (as it may) numerous errors of commission and omission, we feel that at least it serves to summarize the outstanding contribution on a subject that has received but scant attention in the United States.

"The results of purely scientific investigations on wood chemistry have been stressed and we have attempted to point out the many gaps and loopholes in our present knowledge. This has led us occasionally to indicate what new avenues of investigation might profitably be opened in the future. In the case of moot questions, we have attempted to present the experimental data and to discuss the viewpoints of the various investigators open-mindedly. On the other hand, we have consistently attempted to differentiate between *speculation* and *investigation*."

Under "Chemical Components of Wood" the chapters are entitled: cellulose, the principal constituent of the cell wall; polysaccharides of wood; lignin; lignin derivatives and the constitution of lignin; extraneous components of wood. Under the general heading of "Proximate and Summative Analysis of Wood," we find the chapters: introduction; the sampling of wood—miscellaneous determinations; the determination of cellulose; the determination of pentosans and hexosans in wood; the determination of lignin; analytical data and their significance. Under "Decomposition of Wood" we have the chapters: combustion of wood; the decomposition of wood by heat; hydrolysis of wood; delignification of wood; decomposition by concentrated alkali. The last section deals with "Wood as an Industrial Material" and has only the two sub-heads: physical properties; the deterioration of wood.

"Different hypotheses regarding the size of the cellulose molecule have also appeared in the cellulose literature. Views on this subject may be briefly summarized as follows: (a) a relatively enormous molecule made up of a great number of anhydrodextrose residues, many of which go to make up the anhydrocellobiose linkages referred to above; (b) a large aggregate made up of comparatively small units, each one of which contains the anhydroglucose linkage a relatively small number of times. The units are held together in the larger aggregate by means of secondary valence or in some similar way which is not yet fully determined. From the work of Herzog and his co-workers it appears that the cellulose aggregate is crystalline.

"The viewpoint outlined under (a) although held by individual investigators, has been largely displaced by that referred to under (b)," p. 25.

"Perhaps the most modern and generally accepted concept of lignification has been formulated by Wislicenus. Realizing that lignin could not be considered a definite compound, and that the analytical data on lignin varied with nearly every investigator, Wislicenus undertook a dynamic study of lignin formation. He determined the content of adsorbable (colloidal) matter in the cambial saps of a number of trees by treating a given volume of sap with some substance like alumina, and determining the amount of adsorption by comparing the residue obtained by evaporating the treated sap to dryness, and subtracting this residue from that obtained by evaporating an equal volume of untreated sap. These data led him to believe that the period of maximum colloid content of the sap coincided with the period of most rapid and intensive growth. As a result he enunciated the sweeping hypothesis that lignin is composed of the sum total of colloiddally dissolved hydrosols (of high molecular weight) which are deposited by adsorption from the formative (Bildungs) or cambial sap upon the surface of the cellulose fiber, the synthesis of which precedes lignification. While the assumption is made that adsorption is primarily responsible for lignification, the possibility of chemical interaction between certain components of the heterogeneous lignin and the cellulose gel is not excluded. Wislicenus was careful to make his hypothesis broad enough to include both the older encrustation theory by Payen, and the chemical compound theories of Hoppe-Seyler, Lange and Grafe," p. 48.

"The cause of the colorations has been attributed to various components of the wood. Since the colorations disappear after the wood has been treated with NaHSO_3 or with hydroxylamine, the reactions have often been associated with aromatic aldehydes. Czapek was able to remove from wood a very small amount of substance, apparently an aldehyde, which still gave all the color reactions of the original wood. This substance, which was removed by heating wood with ZnCl_2 and extracting this solution with C_6H_6 or ether, he termed *hadromal* but he was never able to isolate it in sufficient amount to permit its complete identification. This hadromal could not have represented more than a small fraction of that part of wood which is ordinarily termed lignin, and Czapek's work clearly showed (what a number of other investigators had suspected) that the brilliant lignin color reactions were really due to a minor constituent of the wood. This was confirmed by Crocker who showed that both oil of cloves and oil of sassafras gave colorations with phloroglucinol and with aniline. The absorption spectra of these colored substances were identical with those of the corresponding substances obtained by the interaction of the same reagents with wood. In other words, the substance in wood that is responsible for the coloration is also present in small amount in certain essential oils. Crocker's results show that the color tests do not characterize any appreciable part of the lignin. They are apparently indicators of a small amount of an aldehyde (coniferyl aldehyde?) which normally accompanies the lignin fraction," p. 50.

"In demonstrating some of the striking analogies between the behavior of coniferyl alcohol and lignin of spruce wood, Klason pointed to the fact that both of these substances give similar *aromatic* compounds when fused with alkali. This finding has lent support to the fairly general belief that an aromatic nucleus is preformed in lignin, since it has been shown repeatedly that the fusion with alkali of various lignin fractions and lignin derivatives gives rise to protocatechuic acid and pyrocatechol, besides the so-called indefinite "lignic" acids and oxalic acid. A thorough investigation of this fusion was made by Heuser and Winsvold and later by Heuser and Hermann. The former also give an excellent résumé of the literature. Heuser and Hermann showed that when the KOH fusion of a lignin fraction (isolated from spruce by means of hydrochloric acid) was carried out (in nickel dishes) in air, at 240° - 250° , the products were largely the "lignic acids," and oxalic acid, while the yields of crude protocatechuic acid and pyrocatechol were 16.4 and 3.7 per cent respectively. They also showed that the pyrocatechol was a secondary product formed from the protocatechuic acid, and that when the fusion was carried out in hydrogen (in place of air), the oxalic acid yields dropped considerably (sometimes to the vanishing point). When an iron crucible replaced the nickel crucible in the fusion, and an atmosphere of hydrogen was used, no oxalic acid was obtained but the pyrocatechol yield rose to 21 per cent, and about 10 per cent of the crude protocatechuic acid was formed. If, however, the fusion was

carried out in iron, an atmosphere of hydrogen, and in the presence of ammonium carbonate, 23 per cent of crude protocatechuic acid, and only 7 per cent of pyrocatechol were formed, with no change in the "lignic acid" yield and without production of oxalic acid. They showed definitely that the fusion of cellulose with KOH yielded neither protocatechuic nor pyrocatechol, irrespective of whether they used iron or nickel crucibles or carried out the fusion in air or hydrogen. In nearly all cases they obtained about 90 per cent oxalic acid, besides appreciable amounts of acetic acid and small amounts of formic acid. Evidently the oxalic acid formation from cellulose was not due to oxidation. Later Heuser and Roth showed that xylan on alkaline fusion yielded only traces of aromatic compounds and that these could be attributed to the presence of impurities in the material used," p. 58.

"While the coloring principles and dyes in plants are usually associated with the leaf and flower, and are largely absent from fruits, roots, bark, and wood, there are cases in which the woody tissue is unusually rich in these substances. Classical examples are the brazilwoods and logwood; and other examples, such as the wood of "old fustic," osage orange, and young fustic, might be cited. Some of the dyestuffs thus obtained from wood are still commercially valuable, although the importance of others has receded with the growth of the synthetic dye industries.

"In many cases the dye itself is not preformed in the wood, and its precursor (i.e., the coloring principle) may be extracted from the finely divided wood by means of ether, alcohol, or water, or by a succession of solvents. The coloring principles are therefore not a part of the cell wall but must be grouped with the extraneous substances of wood.

"The most important commercial dyestuff is obtained from logwood (Campeche wood, *Haematoxylon campechianum* L.), a tree which is indigenous to South America and the West Indies and which belongs to the *Cesalpinae* group of Leguminosae. . . . Logwood is widely used in producing "blacks" on wool, silk, and (to a lesser extent) on cotton. It is one of the few natural dyestuffs that has withstood the competition of the synthetic dyes," p. 100.

"The East Indian satinwood (*Chloroxylon Swietenia*) contains a crystalline substance, chloroxylonine, $C_{22}H_{27}NO_7$, m. $182-3^\circ$, which appears to be responsible for the dermatitis caused by the action of the sawdust of this wood. The Central American cocobolo wood (*Dalbergia* spp.) used in the manufacture of knife handles in the U. S., also exhibits toxic properties that may be due to the presence of an alkaloid, the nature of which remains undetermined. Another alkaloid, also unidentified, is a component of the wood of an inferior type of Knysna boxwood of Kamassi wood grown in Southeast Africa. This substance is a heart depressant and resembles the curare-arrow poison in its action.

"Occupational diseases due to the poisoning caused by these and other woods depend on the sensitiveness of certain individuals to the toxic substances in the wood. The suggestion has been made that only laborers immune to such poisons be selected for work in the industries utilizing cocobolo, satinwood, etc," p. 118.

"As we will see in the next chapter, wood begins to decompose at about 275°C . and that decomposition is exothermic in character. During the course of this decomposition combustible and incombustible gases and vapors are formed, and a combustible residue, is left behind. Since there is no considerable decomposition of wood below this temperature, it would not be expected that the wood could ignite sooner because the oxygen of the air certainly could not combine directly with the solid wood substance at such low temperatures. The ignition temperature of all woods would be expected to be at about 275°C . under the optimum conditions. This theory probably holds except (1) as the physical properties of the wood, such as porosity, influence the surface of contact between the wood and air and (2) for the presence of extractives with low ignition temperatures, such as volatile oils. If the ignition takes place at about 275°C . it means that the vapors or gases formed by the decomposition of wood by heat normally ignite at this temperature or that they ignite at a lower temperature than usual due to the catalytic action of the residue of charcoal, or else it means that the exothermic heat carries the temperature locally above 275°C . and starts the combustion. The ignition temperature cannot be much above 275°C .

because if so it would be possible to distil wood to a residue of charcoal in the open air without combustion which seems impossible when the ready ignition of freshly formed charcoal is considered," p. 187.

"The combustion of wood may be considered to take place in two stages: 1st, the combustion of gases and vapors given off by the exothermic decomposition of wood and 2nd, the combustion of the solid residue of charcoal left behind after the exothermic reaction is finished. These stages may not be sharply defined, since volatile combustible material is driven off from the original charcoal if it is further heated after the completion of the exothermic reaction but there is certainly a change in the character of the combustion at about this time. This is further indicated by the fact that about half the vapors and gases given off during the exothermic reaction are incombustible (CO_2 and H_2O), while nearly all the gases given off afterwards are combustible. It can readily be conceived therefore that the outside of a large stick of wood may be heated to the ignition temperature and burn through the first stage of combustion without heating the interior of the stick above 275°C . On account of the low conductivity of charcoal, the heat from the combustion of the charcoal on the outside of the stick may not be conducted inward rapidly enough to heat more wood to the distilling point and the "fire may go out." This accounts for the difficulty in burning large chunks of wood, such as stumps or logs, unless the conditions are such as to keep the heat from being radiated away. A large pile of stumps may be burned without much difficulty but the burning of a single stump is a hard job. One piece of wood keeps another afire.

"This property of burning rapidly on the outside, charring a thin layer, and then being extinguished entirely or burning very slowly is a valuable one for wood used for construction work exposed to fire hazards. In fact steel under the same conditions and carrying the same load may be rapidly heated through and not infrequently may lose its strength and drop its load sooner than the wooden member," p. 188.

"At one time the ashes obtained by the combustion of wood were of considerable importance as a source of potash; in fact it is hardly a century ago that in newly settled localities in this country the chief value of wood lay in its potash content. The pioneers in clearing their land piled the logs until they were dry enough to burn and after burning carefully collected the ashes. This was frequently the first valuable product from the land and the only one with a cash value. For many years after this period wood ashes were sufficiently valuable to pay for their collection and use as fertilizer or as a source of crude potash. Perhaps even today some home-made soft soaps require the saving and leaching of ashes from the farmer's stove.

"Since the commercial production of potassium salts from the Stassfurt deposits, the value of wood ashes has diminished and they are no longer an article of commerce. In most places where large amounts of wood are burned as in sawmill power plants or in waste burners, the draft through the fire-box is so rapid that the ashes go out with the smoke. Where wood is used in small amounts as for domestic fuel the cost of collection of the ashes is prohibitive," p. 193.

"There is no apparent relation between the physical properties and chemical composition of pulps. It is known that certain cooking conditions produce pulps with certain desirable properties and in general the well-cooked pulps rather than the under-cooked possess the better properties, but the corresponding differences in chemical composition are unknown. The more complete cooking may, of course, leave a smaller residue of lignin in the pulp but it is not likely that the presence of more or less lignin within low limits has any direct bearing on strength. The weakness of certain over-cooked or burned pulps is probably due to slight and obscure chemical changes such as those that take place in drying or steaming wood at temperatures just above 100°C ," p. 254.

"The exact requirements of the cellulose to be used in making cellulose esters are not known. There are specifications for the cotton cellulose used for this purpose but perhaps wood pulps might be satisfactory which did not comply with these specifications. Since a different set of impurities are to be guarded against in the case of wood pulps, a different set of tests should be prepared. It is known that sulfite pulps from spruce are being used

in making viscose and it has been reported that wood pulps have been successfully used for nitration but the detailed effects of variations in composition on the properties of the esters have never been published. If small pentose and mannose yielding residues are not harmful and if either a little color or a slightly higher alkali solubility can be allowed, then wood pulps can be readily prepared for use in making cellulose esters," p. 262

"The ease with which liquids can be forced into wood is of interest chiefly in connection with preservative treatments or with chemical reactions like the pulping processes where it is desired to bring the reagent into contact with all parts of the chip. Most of the available data were obtained in experiments in treating wood with coal-tar creosote. There is very little correlation possible between penetrability and structure and there are several conflicting theories as to just how creosote or other liquids pass into and through wood under pressure. We will, therefore, state the generally accepted facts in regard to treatment with creosote and leave the details of experiments and theory to the special literature on the subject.

"The penetration of creosote into wood under pressure is very much greater in the longitudinal direction than in either of the other directions and there is commonly little difference between radial and tangential penetration. Sapwood is commonly easier to treat than heartwood. Summerwood is commonly easier to treat than springwood, especially in softwoods. Dry or partly dry woods are easier to treat than green woods. There is a wide variation in the ease of penetration of different species.

"There is one satisfactory relation between structure and penetration. Red oaks, for instance, are very easily penetrated in the longitudinal direction through the pores, while white oaks with very similar structure are very difficult to penetrate. This difference is due to the fact that the pores of white oak are obstructed by peculiar, thin-walled, irregular, growths called tyloses. In wood with pores not obstructed by tyloses the longitudinal penetration takes place through the pores but in hardwoods with obstructed pores, the path of the liquid is a subject of controversy. The debate hinges on whether or not the membranes of the bordered pits are perforated, permitting liquids to pass from one tracheid to another.

"Obviously, there is a great need for further information on the mechanism of the passage of liquids through wood. Much of this information may be obtained by purely structural, microscopic studies, but further information is also required on the transfusion of liquids absorbed in the cell wall which may be called a physical or physicochemical study," p. 280.

The authors are apparently not aware, p. 302, that in some cases of blue wood the color is a structural and not a pigment blue.

Wilder D. Bancroft

Physikalisch-chemische Metamorphose. By Ernst Cohen. 28 X 16 cm; pp. 135. Leipzig: Akademische Verlagsgesellschaft, 1927. Professor Cohen was the first non-resident lecturer at Cornell under the gift from Mr. George F. Baker. These lectures were first published in English (31, 1593) and now appear in German, reversing the usual order.

Wilder D. Bancroft.

A Text-Book of Inorganic Chemistry. By Fritz Ephraim. Translated by P. C. L. Thorne. 24 X 17 cm; pp. 807. London: Gurney and Jackson, 1926. Price: 28 shillings. The German edition was reviewed in 1924 (28, 302). We welcome an English edition because it is at present very difficult for students to get a reading knowledge of German at school. This translation is based on the third German edition.

Wilder D. Bancroft.

FIRST REPORT OF THE COMMITTEE ON PHOTOCHEMISTRY,
DIVISION OF CHEMISTRY AND CHEMICAL TECHNOLOGY,
NATIONAL RESEARCH COUNCIL

BY H. S. TAYLOR

The following six papers represent the initial effort of the Committee on Photochemistry¹ of the Division of Chemistry and Chemical Technology of the National Research Council to promote further interest in the problems of photochemistry. During the last two decades the subject has undergone a considerable expansion consequent upon the adoption of newer ideas in the realm of physics with respect to the nature of light, and the processes of its absorption by atoms and molecules. The concept of quanta of light and of quantised absorption by atomic and molecular species has led to an entirely different attitude towards photochemical problems from that which was held in the first decade of the present century. The acceptance of the quantum theory has been more complete upon the part of physicists than by chemists and among the latter there still remains a degree of conservatism with respect to the older concepts.

The attempt has been made in the articles which follow to discuss some of the problems of photochemistry from both standpoints. In the article by Professor Bancroft will be found an exposition of what might be termed the classical attitude to photochemical work. On the other hand the modern physical point of view with respect to the absorption process and the changes produced in the absorbing system by the energy absorbed has been stated in its pertinent aspects by Professor L. A. Turner of the Physics Department of Princeton University. The quantum concept, in its relation to the chemical reactions occurring, has formed the subject of Professor Taylor's contribution. Since all quantitative photochemical work must eventually involve the measurement of light absorption and the quantitative evaluation of light energy incident to the photo-system, this problem has been very comprehensively treated by Professor G. S. Forbes and by Dr. H. de Laszlo. The subject of photochemistry has much in common with the production of chemical reactions by alpha-particles and by other sources of ionisation. This forms the subject of a final article by Professor S. C. Lind.

The whole group of contributions is offered in the hope that progress in photochemical research in the United States may be stimulated by their perusal. It is planned to follow this report by others which deal more extensively with particular problems in the field.

¹ The Committee is composed of the following members: Professors W. D. Bancroft, G. S. Forbes, S. C. Lind, F. Daniels and H. S. Taylor, *Chairman*. The articles which follow have not been submitted to the Committee as a whole. The individual authors are alone responsible for their respective contributions.

EXPERIMENTAL TECHNIQUE FOR QUANTITATIVE STUDY OF PHOTOCHEMICAL REACTIONS*

BY GEORGE SHANNON FORBES

Introductory. Experimental photochemistry is such a many-sided subject that the scope of this paper must be severely restricted. It deals with chemical reactions evoked by light from external sources, and from the red to the beginning of the Schumann region. Heterogeneous systems are not discussed.

Photochemical literature is burdened with an unduly large proportion of articles which are useless or misleading because part only, if any, of the essential variables were measured. Photochemical generalization, for insufficiency of sound experimental data, is still uncertain regarding many vital matters. Only consistently quantitative methods can banish the dubious hypotheses which the pseudo-quantitative type of paper engenders.

In what follows, therefore, the emphasis is placed upon monochromatic procedures, in which both energy absorbed and substance transformed are adequately measured. It will be evident that a considerable degree of accuracy is compatible with reasonable simplicity and economy. The treatment is in no sense historical or encyclopaedic, but rather selective and critical; the same is true of the bibliography, which includes less than a third of the papers which received more than passing consideration.

Sources of Information. Most details are given by reference; also whole topics when connected and satisfactory expositions are accessible. A dagger indicates a reference list of importance. Grateful acknowledgment is made of assistance rendered by Mr. R. M. Fuoss in connection with the library work.

It will be recalled that the Research Information Service of the National Research Council, Washington, D. C., "places at the immediate command of individuals, institutions and firms, information concerning scientific instruments, apparatus, lantern slides, laboratory construction and equipment, bibliographies and reference lists both published and unpublished, research problems, projects, methods, funds, personnel and other subjects of interest to investigators." It will also give the names of dealers, domestic and foreign, which can supply specified instruments and apparatus. Many dealers, in turn, are glad to send reprints, folders or booklets on the theory and use of photochemical instruments.

* Contribution from the Chemical Laboratory of Harvard University.

General References

"Ueber den Energieumsatz bei photochemischen Vorgängen." E. Warburg: *Sitzungaber. preuss. Akad. Wiss.*, 1911, 746; 1912, 216; 1913, 644; 1914, 872; 1915, 230; 1916, 314; 1918, 300; 1918, 1288; 1919, 960; *Z. Elektrochem.*, 26, 54 (1920); 1927, 133 (1921). The foundation of quantitative photochemistry.

^{10b} "Optische Methoden der Chemie," F. Weigert. Akad. Verlagsges., Leipzig (1927). The best summary of the field.

¹¹ "Arbeitsmethoden der Photochemie," G. Jung. "Handbuch der Arbeitsmethoden in der anorganischen Chemie," 2 II, 1477-1560. Edited by Tiede and Richter. Walter de Gruyter and Co., Berlin and Leipzig (1925). Modern and scholarly, includes quantitative details.

¹² "Hand- und Hilfsbuch physiko-chemischer Messungen," 682-739. Edited by Drucker. "Akad." Verlagsges., Leipzig (1925). Elementary, but deserving of careful study.

¹³ Photochemische Versuchstechnik, J. Plotnikow. Akad. Verlagsges., Leipzig (1912). Still of value in qualitative work.

¹⁴ "Lehrbuch der Photochemie," J. Plotnikow. Walter de Gruyter and Company, Berlin and Leipzig (1920). Brief on the experimental side.

¹⁵ "The Chemical Action of Ultraviolet Rays." Ellis and Wells. Chemical Catalog Co., Inc., New York. An extended survey of the qualitative side of the subject.

¹⁶ "Ultraviolet Radiation." M. Luckiesh. D. Van Nostrand Co., (1922). Less comprehensive but more critical and quantitative than ¹⁵.

¹⁷ "Die Lehre von der strahlenden Energie," G. Schmidt, in Chwolson's Lehrbuch der Physik, 2 II. Vieweg and Son, Brunswick (1922). Helpful in radiometric work.

¹⁸ "Die Lehre von der strahlenden Energie" (Optik), O. Lummer, in Müller-Pouillet's Lehrbuch der Physik, 11th Edition. Vieweg and Son, Brunswick (1926). Authoritative and up-to-date in optics. Light production and radiometry are not included.

¹⁹ "Experimental Optics," G. F. C. Searle. Cambridge University Press (1925). Clear, practical and complete enough for photochemists.

²⁰ "Dictionary of Applied Physics," 4, R. Glazebrook. Macmillan (1923). Not written primarily for the photochemist.

²¹ Photochemistry, 1914-1925. A. J. Allmand. Annual Reports on the Progress of Chemistry, London (1926). The best summary of the period. Does not discuss experimental methods.

²² A Review of Photochemistry, W. A. Noyes, Jr., and L. S. Kassel. Chem. Reviews, 3, 199 (1926). Less comprehensive than ²¹.

²³ "Photochemie und Photographie," 1, K. Schaum. J. A. Barth, Leipzig (1908).

²⁴ "Photochemistry." S. E. Sheppard. Longmans, Green and Co., New York (1914).

²⁵ "Lehrbuch der Chemie," 3, 865-883. M. Trautz. Walter de Gruyter and Co., Berlin and Leipzig (1924). Not detailed regarding experimental methods.

²⁶ "Spectroscopy," 2, E. C. C. Baly. Longmans Green and Co., New York (1927).

Light Sources. (General). The ideal photochemical light source is extremely intense and concentrated, and should be efficient, convenient and economical. Much of its total energy is radiated through a relatively small number of lines ²⁷ evenly spaced in the actinic region. The continuous background should be relatively weak. It should be shaped like a monochromator slit, and better still have the same dimensions. Rapid variations in intensity about a constant mean value can usually be tolerated, and evenly progressive changes invite interpolation, but violent fluctuations are incompatible with quantitative work. A concave mirror behind the source ²⁷ or a projection apparatus ²⁸ increases the intensity of illumination. Mirrors can reflect radiation upon the sides of the vessel ²⁹ and a mirror placed behind the vessel multiplies absorption by a factor between 1 and 2 ^{124, p. 284}. A weak or unsuitable source takes such heavy toll in time spent and in quality of results, that economy is the worst form of extravagance. The permissible minimum of light intensity is discussed below under "Analytical Methods."

References^{1, 2, 11, 12, 13, 15, 16, 23, 24, 120a}

²⁷ "Handbuch der Spectroscopie," 7, Kayser and Konen. S. Hirzel, Leipzig (1924).

²⁸ Noddack: Z. Elektrochem., 27, 359 (1921).

²⁹ Kiss: Rec. Trav. chim., 42, 665 (1922).

³⁰ Plotnikow: Z. wiss. Phot., 21, 103 (1921).

Sources with approximately Continuous Spectra

Sunlight^{16, pp. 15-34} costs nothing, and is extremely intense in the visible, especially at high altitudes^{16, pp. 17-22} or in the tropics^{30, 31}. Its spectrum, which practically terminates at $300m\mu$ ^{16, p. 24} is for photochemical purposes best imitated by the blue gas-filled tungsten lamp,^{16, p. 117} or by the snow-white flame arc.³² Combinations of the mercury vapor lamp with various thermal radiators are its equivalent for color-matching only.³³ The mercury vapor lamp with a crown-glass filter is said to behave like sunlight in fading tests.³⁴ Lenses or concave mirrors concentrate sunlight further, and water filters^{16, p. 49} mitigate the thermal effect. The extreme variability of sunlight,³⁵ the need of a heliostat^{18, pp. 114-117}, and the fact that its spectrum is continuous, except for the dark lines, all handicap quantitative monochromatic work. Such drawbacks, however, must not discourage further investigation of its immense possibilities.

³⁰ Dhar and others: *J. Chem. Soc.* 123, 1856 (1923).

³¹ *J. Phys. Chem.*, 29, 926 (1925).

³² Mott: *Trans. Am. Electrochem. Soc.*, 28, 371 (1915).

³³ Ives: *Bur. Standards Sci. Paper*, 271 (1909).

³⁴ Flynn: *American Dyestuff Reporter*, 12, 293, 837 (1923).

³⁵ Coblenz and Kahler: *Bur. Standards Sci. Paper*, 378 (1920).

Solid Radiators^{16, pp. 107-104}. Incandescent filaments, straight or coiled, should, if used with a monochromator, approximate the dimensions of the slit. The thin glass bulb transmits much ultraviolet, and a quartz window³⁶ can be added. Overloading greatly increases the ultraviolet output,³⁶ though shortening the life of the lamp. The Nernst glower³⁷ is still made by the Glasco-Lampen Gesellschaft, Berlin; a laboratory recipe has been published,³⁸ its spectrum is very faint beyond $250m\mu$ ^{16, p. 109}. "Glowbar" is useful for infrared work only. If magnesium^{24, p. 102} could be fed uniformly into oxygen over a considerable period, it would be of greater value.

Flames of burning gases are infrequently used in photochemical work. Considerable ultraviolet is emitted by acetylene properly burned in oxygen^{24, p. 101} and by the carbon disulfide-oxygen lamp^{39, 40}.

High Tension Discharges under Water^{15, pp. 24-6} between electrodes of aluminum, brass, tungsten, etc., from a step-up transformer coupled or not with a Tesla coil produce spectra continuous to $210m\mu$. Such sources are more valuable for photographic work^{41, 42} on absorption spectra than for photochemical reactions.

³⁶ Gelhoff: *Z. tech. Physik.*, 1, 224 (1920).

³⁷ Coblenz: *Bur. Standards Bull.*, 9, 103, 109 (1913).

³⁸ Griffiths: *Phil. Mag.*, 50, 263 (1925).

³⁹ Wulf: *Ann. Physik*, 9, 946 (1902).

⁴⁰ Tassily and Gambier: *Compt. rend.*, 151, 342 (1910).

⁴¹ Tyndall: *Bur. Standards Tech. Paper*, 148 (1920), Appendix.

⁴² Gibson: *Bur. Standards Sci. Paper*, 440 (1922).

Sources with Discontinuous Spectra

Arcs¹⁵, pp. 27-29; 16, pp. 107-164, excepting flaming arcs, are not well shaped for use with slits. Feeding mechanisms allow considerable fluctuations. The ordinary carbon arc's spectrum is weak beyond $250\text{m}\mu$ ¹⁶, p. 107. The spectral energy distributions in crater and flame are unlike, and the lines are disadvantageously spaced. Bassett⁴³ has studied carbon arcs carrying several hundred amperes. Carbon electrodes can be cored or impregnated¹⁶, p. 124. The flaming arc has been carefully studied, especially by Mott⁴⁴, 45. Of many metals, copper, cadmium, iron and tungsten are most frequently employed as electrodes. King⁴⁶, 47 has operated arcs between metallic rods with 1000-2000 amperes, producing normal and enhanced spectra in great intensity. The copper arc of Meyer and Wood⁴⁸ gives radiations of very short wavelength. W. Taylor^{49a} found the "Pointolite" lamp very intense in the visible.

⁴³ Bassett: *Trans. Am. Electrochem. Soc.*, 44, 153 (1923).

⁴⁴ Mott: *Trans. Am. Electrochem. Soc.*, 31, 365 (1917).

⁴⁵ *Trans. Am. Electrochem. Soc.*, 37, 665 (1920).

⁴⁶ King: *Astrophys. J.*, 62, 238 (1925).

⁴⁷ *Science*, 65, January 7, supplement 10 (1927).

⁴⁸ Meyer and Wood: *Phil. Mag.*, 30, 449 (1915).

^{49a} W. Taylor: *Phil. Mag.*, 49, 1166 (1925).

Sparks between metallic electrodes are almost indispensable for work below $250\text{m}\mu$. Warburg's zinc sparks^{10a}, p. 135 gave at $254\text{m}\mu$ a thousand-fold the intensity of his mercury vapor lamp. The elements of the second and third groups give advantageous spacing of lines.²⁰ Many papers on the subject have accumulated⁴⁹, 16 pp. 140-144 but more data on absolute spectral intensities under specified conditions would be welcomed by photochemists. Warburg¹, 2, 6, 10, Lenard and Ramsauer¹¹, p. 1521, also others⁵⁰, 163, 203 have described adequate installations. Many such outfits¹⁵, pp. 22-4 are underpowered. A transformer consuming several K.W. and yielding at least 20,000 volts should be used. Special wiring may have to be run through the building. Mica condensers are better than Leyden jars. Warburg¹ housed his spark gap in a chamber with a quartz window and an air-blast. He threw its image on a screen, and kept it constant by a feed worked by a glass rod,² but intensity varied 3-6%.⁶ Harrison and Hesthal⁶¹ combatted unsteadiness by rotating the lower electrode, and by regulating the gap and the primary impedance. Kowalski^{51a} by adjusting the capacity, brought the greatest intensities into the middle ultraviolet.

⁴⁹ Pfüger: *Ann. Physik*, 13, 904 (1904).

⁵⁰ Henri: "Etudes de Photochimie," 9. Gauthier-Villars, Paris (1919).

⁶¹ Harrison and Hesthal: *J. Opt. Soc. America*, 8, 472 (1924).

^{51a} Kowalski: *Compt. rend.*, 158, 1337 (1924).

Mercury Vapor Lamps of fused quartz approximate the ideal light source in so many respects that most photochemists use them. Numerous modifications are described¹⁵, pp. 30-30. The cathode is always of mercury, the anode of mercury or of tungsten. In the latter case reversal of polarity must be avoided. The commercial lamps have sealed-in electrodes, and not all of them

can be operated in both a horizontal and a vertical position. For alternating currents a rectifier is ordinarily used instead of a three-electrode lamp, but a two-electrode lamp for high frequency has been described.⁵³ The manufacturers supply detailed directions for operation. A lamp with sealed-in electrodes is slow to attain a steady state. Light intensity varied with line voltage and ventilation. They will not stand heavy overloading. First cost is high, and freshening, when the ultraviolet transmission has deteriorated^{53, 54, 120a, p. 54⁶}, is expensive in time and money.

The unsealed constant-pressure lamps recently described avoid the above difficulties^{55, 56, 57, 58}. The disadvantages of heavy overloads are relatively small. Dr. P. A. Leighton of this laboratory has constructed an open lamp water-cooled and with adjustable pressures which can maintain for hours galvanometer deflections constant within a fraction of a percent. When extreme concentration of light is not required, the bore of the constricted arc should be four rather than two millimeters.⁵⁹ The ends of the luminous column should not be opposite the slit. The constriction can be bent to match a collimating slit curved to neutralize distortion of the beam at the exit slit. The constriction can be omitted and the lamp immersed in a tank so that the water level stands about a centimeter below the slit. The capillaries used to restrain oscillations⁵⁶ can be made quite large if blocked with steel wires. A powerful air-blast can replace water cooling.⁵⁹ Fuses afford protection against short circuits caused by collapse of the luminous column.

The recently invented mercury vapor induction lamp devised by Foulke⁶⁰ has great possibilities for photochemistry. It has no electrodes, but the vapor is excited by a rapidly changing electromagnetic field. Intensity is greatly increased by small amounts of inert gas, as is the case with lamps having electrodes.⁵² A lamp of 10 cm. radius run on 2.5 K.W. gave a horizontal candle power of 20,000. Unfortunately the cost of installation is considerable.

⁵³ George: *Rev. d'Optique*, 4, 82 (1925).

⁵⁴ Coblenz, Long and Kahler: *Bur. Standards Sci. Paper*, 330 (1918).

⁵⁵ Reeve: *J. Phys. Chem.*, 29, 39 (1925).

⁵⁶ Harrison and Forbes: *J. Opt. Soc. America*, 10, 1 (1925).

⁵⁷ Forbes and Harrison: *J. Opt. Soc. America*, 11, 99 (1925).

⁵⁸ Forbes and Harrison: *J. Am. Chem. Soc.*, 47, 2449 (1925).

⁵⁹ Forbes and Leighton: *J. Phys. Chem.*, 30, 1628 (1926).

⁶⁰ Villars: *J. Am. Chem. Soc.*, 49, 326 (1927).

⁶¹ Foulke: *New York Regional Meeting of the A.I.E.E.*, Nov. 11 (1926).

Vapor Lamps with Other Metals^{15, pp. 66-8}. Stark and Kűch⁶¹ tried out melted cadmium, zinc, lead, bismuth, antimony, tellurium, selenium. Lowry and Abrams⁶² used solid cadmium. To avoid breakage Sand⁶³ added zirconia, and Bates⁶⁴ gallium. Sodium-potassium alloy has been used.⁶⁵ Amalgams contain such ingredients^{13, p. 14; 16, p. 150; 66} as cadmium, zinc, thallium and caesium to enrich the spectrum; the added metal collects at one pole or on the walls, and inconstancy results.⁶⁷ The Bates lamp would seem to be the most intense, steady, and practical of this group. Dr. George K. Burgess of the Bureau of Standards, in a private letter to me stated that all the cadmium lines including those in the region 250 $m\mu$ to 185 $m\mu$ can probably be obtained with greater intensity from this lamp than from any other source.

Precautions. Although the dangers of ultraviolet light have been minimized,⁶⁸ all will agree that high-grade welding goggles^{69, 70, 15 pp. 72-76} with sides must be worn near a powerful source. It will pay to buy a light and a dark pair. Avoiding lateral exposure, ordinary spectacles afford some protection. Welding masks, gauntlets, and aprons follow goggles as exposure becomes more severe. Ellis and Wells discuss^{15, p. 290} susceptibility, with emphasis upon diabetes. A ventilated lamp-house with heavy red glass windows protects the experimenter and keeps ozone out of the room. Rubber is shellacked or wound with electric tape. A paint of zinc oxide and lampblack absorbs stray radiations.⁷¹

⁶⁸ Stark and Ktich: *Physik. Z.*, 6, 438 (1905).

⁶⁹ Lowry and Abrams: *Trans. Faraday Soc.*, 10, 103 (1915).

⁷⁰ Sand: *Proc. Phys. Soc. London*, 28, 94 (1915).

⁷¹ Bates: *Bur. Standards Sci. Paper*, 371, 45 (1920).

⁶⁸ Newman: *Phil. Mag.*, 44, 944 (1922).

⁶⁹ Callier: *Ann. Physik.*, 33, 1061 (1910).

⁷⁰ von Halban and Siedentopf: *Z. physik. Chem.*, 103, 73 (1922).

⁷¹ Verhoef and Bell: *Science*, 40, 453 (1914).

⁶⁸ Gibson and McNicholas: *Bur. Standards Tech. Paper*, 119 (1919).

⁷⁰ with Tyndall: 148 (1920).

⁷¹ Andrews: *Gen. Elec. Rev.*, 24, 866 (1921).

Spatial Energy Distribution. If the distance exceeds ten-fold the greatest dimension of source or reaction vessel, the inverse square law holds within one percent^{20, p. 422}. Deviations for other conditions have been worked out²⁰. "Distance" is neither to the front face nor to the centre of the mixture^{15, p. 65} but rather to that imaginary surface at which half the total absorption has occurred. Unsymmetrical distribution, as with carbon arcs or incandescent filaments, can be mapped^{20, pp. 429-433; 23, pp. 123-129}. Integrals for various dimensions of source and cell are given^{17, pp. 435-9}. Trümpler⁷² gives a formula for mercury vapor lamps at short distances. The conduction of heat away from the ends of such lamps makes the energy E_a radiated perpendicular to their axis, at the ten-fold distance d , nearly equal to $E/4\pi d^2$ per square centimeter of receiving surface, where E is total energy consumed by the lamp.

⁷² Trümpler: *Z. physik Chem.*, 90, 395 (1915).

Quantitative Variation of Light Intensity at constant distance without changing spectral energy distribution^{16, p. 180, 23, p. 106}. (1) Multiplication of sources^{20, p. 445}. (2) Variation in effective area of source (area is not always proportional to energy transmitted). (3) Punched plates or calibrated wire screens^{10b, p. 136}, in irregular motion.⁵¹ (4) Variation in electrical conditions^{55, 56}. (5) Sector wheel.⁷⁴ Certain objections should be noted,^{75, 21, p. 342; 100 p. 458}. Rapid rotation is often important^{76, 77}. (6) Double neutral wedge.⁷⁸ (7) Polarizer and analyzer.⁷⁹ (8) Oblique plates of glass or quartz (hard to figure quantitatively).

⁷⁴ Davis: *Bur. Standards Sci. Paper*, 511 (1925).

⁷⁵ Coblenz: *Bur. Standards Bull.*, 4, 458 (1908).

⁷⁶ Davis: *Bur. Standards Sci. Paper*, 528 (1926).

⁷⁷ Briers, Chapman and Walters; *J. Chem. Soc.*, 1926, 562.

⁷⁸ Butschowitz: *Chem. Ztg.*, 47, 382 (1923).

⁷⁹ Rosenberg: *Z. Physik*, 7, 18 (1921).

The Reciprocity Law predicts that, with other variables constant, total photochemical effect is proportional to the product of intensity and time. Unless the fraction decomposed is small, it is better to find whether the effect is constant for constant products of intensity and time. The limitations of the "law" have been systematically studied⁷³ for the photographic plate only. Allmand^{21, p. 342} gives a non-critical summary of verifications and violations⁷⁷ reported, 1914-25. He also discusses threshold intensities. Wood,⁸⁰ also Pringsheim⁸¹ report that enormous intensities evoke reactions non-existent with moderate ones. If the "law" does not hold in a given case, light intensity must be defined in stating quantum yields. Also the usual mathematical treatment of the illuminated system would have to be corrected for variation in photochemical efficiency with varying depth in the reaction layer. The need for consideration of dark reactions, induction periods and after effects in studies of the reciprocity law is obvious.

⁸⁰ Wood: *Phil. Mag.*, 43, 757 (1922).

⁸¹ Pringsheim: *Z. Physik.*, 10, 176 (1922).

⁷³ Jones and Huse: *J. Optical Soc. America*, 7, 1079 (1923); 11, 319 (1925).

Quantitative Measurement of Radiation Intensity^{12, pp. 731-4}.

Intensimeters⁸² with Sensitivity Curves.⁸³ Photo-electric cells are now made in America which are practically free from time-lag,⁸⁸ fatigue and deterioration, and with intensity-current curves that are almost linear. These are points of great superiority over older types.⁸⁴ Photo-electric cells are highly selective, but different alkali metals or hydrides have sensitivity peaks at different wave-lengths.⁸⁵ They are most useful as null instruments^{86, 87} in comparing two intensities at the same wave-length.

Fluorometers^{89, 90} are simple and inexpensive though not very precise. Sensitivity curves, and relations between incident and emitted light are given by Winther.⁸⁹

Photographic plates have been studied by Harrison^{51, 91}, who mapped their "characteristic surfaces" generalizing the three coordinates intensity, time and density for each of a number of wave-lengths. The ultraviolet range is increased by bathing with fluorescent oils.⁹² Such data make it possible, by a simple photographic photometer,⁹³ to measure the spectral energy distribution of false light (see below), and to measure absorptions (see Dr. de Laszlo's report).

⁸² Report on Spectroradiometry, *J. Opt. Soc. America*, 7, 439 (1923).

⁸³ Coblenz: *Bur. Standards Bull.*, 14, 507 (1918).

⁸⁴ Krüger and Moeller: *Physik Z.*, 13, 729 (1912).

⁸⁵ Rougier: *Rev. d'Optique*, 2, 133 (1923).

⁸⁶ von Halban and Siedentopf: *Z. physik. Chem.*, 100, 212 (1922).

⁸⁷ Gibson: *Bur. Standards Sci. Paper*, 349 (1919); also *J. Opt. Soc., Am.* 7, 693 (1923).

⁸⁸ General Electric Company, catalogue, 1927. See also Goos and Koch: *Physik Z.*, 27, 41 (1926).

⁸⁹ Winther: *Z. Elektrochem.*, 19, 390 (1913).

⁹⁰ Gyemant: *J. Opt. Soc. America*, 12, 65 (1926).

⁹¹ Harrison: *J. Opt. Soc. America*, 11, 341; ⁹² 113; ⁹³ 157 (1925).

⁹⁴ Büchi: *Z. physik. Chem.*, 111, 269 (1924).

Chemical Actinometers should employ only photochemical reactions which are reproducible, which involve only one phase, and whose photochemical efficiency is known for each of a number of wave-lengths. When speed of reaction falls off with decreasing concentrations, fresh reactants must be substituted. Silver halide paper actinometers are extremely crude devices. The Bunsen¹⁴, p. 373 is not reproducible, the Eder¹⁴, p. 461 forms a precipitate. The uranyl oxalate photolysis,⁹⁴ in spite of complications, has many advantages. It is unfortunate that none of the reactions so carefully investigated by Warburg¹⁻¹⁰ are convenient for general use. Self-integrating actinometry for specific purposes, valid even in polychromatic light, has been exemplified by Dorcas and Forbes.⁹⁵

Photogalvanic Cells involve too many obscure phenomena to promise well as actinometers. None the less some use of them has been made.⁹⁶

Selenium⁹⁷ and Thalofide⁹⁸ cells have sensitivity peaks at the longer wave-lengths, and other drawbacks for photochemical work.

⁹⁵ Dorcas and Forbes: J. Am. Chem. Soc., 49, 3081 (1927).

⁹⁶ Athanasiu: Ann. Phys., 4, 319 (1925).

⁹⁷ Pfund: Phys. Rev., 34, 370 (1912).

⁹⁸ Coblenz: Bur. Standards Sci. Paper, 380 (1920).

Intensimeters practically non-selective^{115, 99; 11, pp. 1534-44} produce thermal or electrical effects. In the thermal group the radiometers with vanes^{100, 101, 102}, torsion radiation balance¹⁰³, thermophotometer¹⁰⁴ and radiocalorimeter^{105, 106} and in the electrical group the microradiometer¹⁰⁷ and radiomicrometer¹⁰⁷ all leave something to be desired in range, or convenience or simplicity of interpretation. The thermopile^{100, 108, 109, 111, 112} and the bolometer^{100, 108; 109, p. 171; 111, 113}, have preempted the photochemical field, and both can be made in the linear or the surface form^{4, p. 875}. The building and operation of the bolometer requires more technical information. The linear thermopile with a very thin quartz window, not exhausted, is robust, convenient and gives a relation almost linear between intensity and galvanometer deflections^{108, p. 59}. For accurate work this relation should be plotted, and the zero kept at a fixed point on the scale. By taking readings in a number of positions and integrating graphically the linear thermopile serves the purposes of the surface form. Following the detailed directions of Coblenz^{100, 108, 109} thermopiles can be constructed and mounted by anybody having good eyes, a steady hand and considerable patience. Full directions for installation and use are given also. Several constructed in this laboratory, 30 to 40 × 1 mm. in area and having resistances between 15 and 20 ohms have given excellent service. They have about two thirds the e.m.f. of the newest Hilger thermopiles and the deflections of the two types stand in a very constant ratio throughout the spectrum. At high intensities, shunt resistance, s , and series resistance, a , are provided. A serviceable relation is $s = p(p - a)/a$, where p is the resistance of the pile. Moll^{110, 114, 115} and Burger have described vacuum thermopiles with exceedingly thin junctions. While too sensitive for ordinary photochemical purposes, they should prove useful in determining the spectral energy distribution of false light delivered by a monochromator.

Galvanometer^{100, p. 415; 108}. With thermopiles described above, a d'Arsonval galvanometer of resistance 15-20 ohms and sensitivity 15 mm/mv¹¹⁰ will be satisfactory. The new loop galvanometers^{116a} are very sensitive. Owing to drift, it is difficult to measure the e. m. f. of thermopiles by potentiometry using the galvanometer as a zero instrument. If a Julius suspension is necessary to eliminate vibration, a heavy slab can be made of reinforced concrete. The scale support is cut from a thick board with the proper curvature, the mirror being at the centre of curvature. Millimeter scales, with numbers written as mirror images, are tacked on. A row of small electric bulbs with a shield of bright tin plate is placed in front.

⁹⁹ Fabry: *J. Opt. Soc. America*, 10, 543 (1925).

¹⁰⁰ Coblenz: *Bur. Standards Bull.*, 4, 391 (1908); ¹⁰¹ 12, 503 (1916).

¹⁰² Marsh, Compton and Loeb: *J. Opt. Soc. America*, 11, 257 (1925).

¹⁰³ Tear: *J. Opt. Soc. America*, 11, 135 (1925).

¹⁰⁴ Plotnikow: *Z. tech. Physik*, 5, 113 (1924).

¹⁰⁵ Bowen, Hartley and Scott: *J. Chem. Soc.*, 125, 1218 (1924).

¹⁰⁶ Bowen: *J. Chem. Soc.*, 123, 2328 (1923).

¹⁰⁷ Johansen: *Ann. Physik*, (4) 33, 517 (1910).

¹⁰⁸ Coblenz: *Bur. Standards Bull.*, 9, 7 (1913); ¹⁰⁹ 11, 131 (1914).

¹¹⁰ Moll: *Physica*, 6, 233 (1926).

¹¹¹ Coblenz: *J. Opt. Soc. America*, 5, 259 (1921).

¹¹² Voege: *Physik. Z.*, 22, 119 (1921).

¹¹³ Abbot: *Astrophys. J.*, 18, 1 (1903).

¹¹⁴ Moll and Burger: *Z. Physik*, 32, 575 (1925).

¹¹⁵ "Photometry," Chapter 11. J. W. T. Walsh, Constable and Co., London (1926).

¹¹⁶ "Notes on Moving Coil Galvanometers." Leeds and Northrup Co., Philadelphia (1925).

^{116a} Mechau: *Physik. Z.*, 24, 242 (1923).

Radiation Standards and their Use. Of the various standard flames described^{117; 17, p. 442} the Hefner lamp^{117, 118, 119, 120} is most often used as a total radiation standard. In defining such standards the assumed value of the black body constant^{117, p. 88} should be mentioned. More convenient are the standard carbon lamps,¹¹⁷ with certificate and directions for standardizing thermopiles, ordered from the Bureau of Standards. Two should be used successively in crucial comparisons. Only standard models of ammeters can be used. In particular, overloading must be avoided. A separate calibration curve may be established for each shunt-series resistance, and then all can be combined into one by proper reduction factors. The conditions of standardization and use must agree closely.

To standardize the thermopile for intensities higher than those corresponding to the highest rated amperage of the lamp at the standard distance of two meters the distance is cut down and another set of readings taken for the same amperages. The deflections at the lower current strengths and the lesser distance are interpolated upon the standard curve, and the corresponding energies incident upon the thermopile are found. The ratios of these to the energies at standard distance with equal currents are averaged. The average ratio times the energy for any other current at the standard distance will give the energy incident upon the thermopile at the shorter distance, and the

energy-deflection curves are extended accordingly. No assumption is made, in the process, concerning the relation between intensity and distance.

¹¹⁷ Coblenz: Bur. Standards Bull., 11, 87 (1914).

¹¹⁸ Boltzmann and Basch: Sitzungsber, Akad. Wiss. Wien, 131 IIa, 57 (1922).

¹¹⁹ Gerlach: Physik. Z., 21, 299 (1920).

¹²⁰ Kussmann: Z. Physik, 25, 58 (1924).

Spectral Energy Distribution of Light Sources^{120a} may be roughly worked out by surface integration of a spectral energy curve taken with a spectroradiometer or monochromator having a narrow slit; correction for slit width must be made^{120b; 121; 115, p. 287}. Corrections for aberrations, reflection, absorption, and scattering in the optical train would be desirable, especially in the ultraviolet. Absurd errors result from uncorrected surface integration of such diagrams made with a wide slit. Fabry and Buisson¹²² measured total energy L transmitted by n different filters, of thickness d (or n different thicknesses of the same filter). They solved n equations of the form $L = A_1 e^{-m_1 d} + \dots + A_n e^{-m_n d}$ for A_1, \dots, A_n the n monochromatic intensities of the original source. Of course m_1, \dots, m_n are determined separately for each filter. It is hazardous to assume that two sources of the same type, especially mercury vapor lamps¹²³, have the same spectral energy distributions even if dimensions, electrical conditions and the like are comparable^{53, 54}. The photochemist seldom needs to know the spectral energy distribution of the source itself, as he is primarily interested in monochromatic intensities at the exit slit of his monochromator or behind filters. Indeed he could interpret the total effect of polychromatic light only as a sum of monochromatic effects¹²⁴. The difficulties of such comparisons will be inferred from a study of the literature^{21, p. 342; 125, 126}.

^{120a} Coblenz, Dorcas and Hughes: Bur. Standards Sci. Paper, 539 (1926).

^{120b} Coblenz: Bur. Standards Bull., 10, 41 (1914); 17, 36 (1920).

¹²¹ Franklin, Madison and Reeve: J. Phys. Chem., 29, 713 (1925).

¹²² Fabry and Buisson: Compt. rend., 152, 1839 (1911).

¹²³ Ladenburg: Physik. Z., 5, 527 (1904).

¹²⁴ Wegscheider: Z. physik Chem., 103, 295 (1923).

¹²⁵ Padoa (and others): Trans. Faraday Soc., 21, 573 (1925); ¹²⁶ Gazz., 56, 164, 375 (1926).

Polychromatic Light acting directly upon a sensitive system produces a total effect which is a highly complicated integral¹²⁴ involving spectral energy distribution of the source, absorption coefficients of reactants, products and perhaps of solvent or other substances, concentrations, thickness of layer, quantum yields, time and temperature. Its chief value is to detect photochemical reactions, sensitizers, catalysts, inhibitors, to study concentration effects involving non-absorbing (dark) reactants, and in some (though perhaps not all) cases to investigate temperature coefficients and the reciprocity law. Some quantitative information may be gained regarding the above by instituting comparisons, throughout which the source, the thickness of the absorbing layer and the concentrations of all absorbing substances are practically constant. Obviously these conditions forbid the transformation, during any experiment, of any considerable fraction of any absorbing substance unless all absorption coefficients are measured, or unless the sensitive reactant

absorbs all the light at all stages of the reaction. On the other hand those who delight in "unimolecular constants" have only to start with a mixture which absorbs but a small fraction of the actinic light.

Quantum Yields in Polychromatic Light may be very crudely estimated as follows: The total radiation incident upon the cell face is calculated from the total wattage of the source and the inverse square law, or from thermopile measurements. Concentration and thickness of layer should be sufficient to insure complete absorption of actinic light. Only one absorbing substance should be present. Some arbitrary fraction of the total radiation can be assumed to be actinic. Better, the actinic region is located by trial with filters of given transmissions, and laid off upon a spectral energy diagram of the source, which must include all the infra-red. The ratio of the two areas times total energy is actinic energy absorbed. Average quantum yield follows from the latter, average frequency, and number of molecules transformed (with correction for dark reaction if any). It must of course be proved that no two spectral regions used cause the reaction to proceed in opposite direction^{127, 128}.

Light Filters^{11, p. 1529-34; 12, p. 694-6}. The sum total of data on light adsorption is very great, but relatively few of the systems would make good light-filters. The substance must be definite, reproducible and fast to light even if warmed up. If colloidal, its absorption coefficient must also be unaffected by dilution, by lapse of time or by any substance added. Many dyestuffs^{129, 130} fail to meet these specifications. If oxidizable, as ferrous solutions¹³¹, it must be covered by a suitable liquid. Transmissions, including the container if any, must be known or determined by the investigator for each wavelength of significance. When data on thin sheets are given, small variations in thickness are serious. The methods and precautions of spectrophotometry are given in Dr. de Laszlo's report. If non-selective intensimeters are to be used behind filters, infra-red transmission must not be forgotten. Keyes¹³² interposes a vacuum cell as a protection against the heat of the lamp. A quartz water cell 1 cm. thick transmits 58% at 945 m μ and 14% at 1190 m μ ¹³³. Coblenz has suggested filters to absorb infra-red completely^{134, 135}.

Spectrograms of light sources taken through filters give little quantitative idea of the transmissions of the latter because it is impossible to make due allowance (except by the method of Luckiesh^{16, p. 182}) for spectral energy distribution of the source¹³⁶, sensitivity curve of emulsion, characteristic curves of the plate at different wave-lengths, and the effects of reproduction processes.

As filters have at best rather broad transmission bands, they should be used with discontinuous sources having strong emission lines nearly coincident with their respective transmission maxima. Some filters have a narrow absorption band which blots out one line of a particular source. The didymium filter, glass¹³⁷ or solution, absorbs the yellow line of the mercury vapor lamp, transmitting the green. Unfortunately such coincidences are rare.

Gaseous Filters^{16, pp. 36-45}. While nitrogen is transparent even at 125 m μ ,^{16, p. 36} oxygen absorbs from 186 m μ ^{16, p. 36}, a fact which prevents the shorter wave-lengths from exerting their striking photochemical effects except at

very short distances from the source^{138, 139}. Calcite, also, has been used to intercept these.¹³⁸ If the ozone formed by mercury vapour lamps is not removed by a gentle current of air, radiations between 230 m μ and 280 m μ will suffer to some extent.¹³⁹ Dr. A. L. Marshall has suggested to the author that mercury in pumps or manometers may introduce enough vapors to cause trouble in working with resonance radiations (1) by opacity (2) through excited atoms. The most useful of the gaseous filters contain bromine and chlorine^{140, 141} or chlorine¹⁴² in quartz and transmit λ_{254} . Villars¹⁴³ finds the Peskov filter more nearly monochromatic.

¹³⁷ Mathews: *Ind. Eng. Chem.*, 15, 885 (1923).

¹³⁸ Baly: *Ind. Eng. Chem.*, 16, 1018 (1924).

¹³⁹ Krüss: *Z. physik. Chem.*, 51, 257 (1905).

¹⁴⁰ Uhler and Wood: *Atlas*, Carnegie Inst. Wash. Pub. (1907).

¹⁴¹ Byk: *Z. physik. Chem.*, 49, 659 (1924).

¹⁴² Keyes: *U. S. P.* 1, 237, 652 (1917).

¹⁴³ Nichols: *Phys. Rev.*, 1, 13 (1893).

¹⁴⁴ Coblenz: *Bur. Standards Bull.*, 7, 655 (1911); ¹⁴⁵ 9, 110 (1913).

¹⁴⁶ Bielecki and Henri: *Ber.*, 46, 3640 (1913).

¹⁴⁷ *Bur. Standards Sci. Paper*, 148, 9 (1920).

¹⁴⁸ Baly and others: *Nature*, 112, 323 (1923).

¹⁴⁹ *Ind. Eng. Chem.*, 16, 1016 (1924).

¹⁵⁰ Peskov: *J. Phys. Chem.*, 21, 382 (1917).

Liquid and Solid Filters^{26, vol. 3}. Lack of space forbids any attempt to review critically the data as a whole. The variety of ultraviolet filters is inferior to that for visible, also the information about them. Certain glass filters and dyes were carefully measured up by the Bureau of Standards^{144, 145} including monochromats for mercury vapor lamps. Commercial filters include Agfa, Corning, Cramer, Fuess, Ilford, Jena, Maison Calmels, Wratten. Potapenko¹⁴⁶ gives complete directions for making gelatine-dye filters. Wood's nitrosodimethylaniline¹⁴⁷ filter transmits the long ultraviolet only. Hood¹⁴⁸ describes glasses with rather extraordinary transmissions. Lists of filters are given in a number of books^{11, pp. 1529-34; 12, pp. 694-6; 15, pp. 78-84; 16, pp. 46-92; 13, pp. 72-75}. Nickel oxide glass (Corning Glass Works) transmits 366 m μ .

¹⁴¹ *Z. Physik*, 18, 235 (1919).

¹⁴² Oldenberg: *Z. Physik*, 29, 328 (1924).

¹⁴³ Villars: *J. Am. Chem. Soc.*, 48, 1874 (1926).

¹⁴⁴ Gibson and others: *Bur. Standards Tech. Paper*, 148 (1920); ¹⁴⁵ *Sci. Paper* 440 (1922).

¹⁴⁶ Gibson: *J. Opt. Soc. America*, 13, 267 (1926).

¹⁴⁷ Gray: *J. Phys. Chem.*, 31, 1732 (1927).

¹⁴⁸ Potapenko: *Z. wiss. Phot.*, 18, 238 (1919).

¹⁴⁹ Wood: *Phil. Mag.*, 5, 257 (1903).

¹⁵⁰ Hood: *Science*, 64, 281 (1926).

Procedures with Light Filters, if qualitative, require no extended comment here. Outfits including lamp, case, also holders for sheet filters and quartz or glass cells are advertised. In the absence of a monochromator, or with cells having large surfaces, a thermopile can be read, in several positions, between filter and cell and behind the cell. If radiometer is non-selective, the infra-red radiation absorbed by the solutions must be considered. Noddack²⁷ de-

scribes a typical apparatus. Correction for reflection^{8, p. 1230} can be made as described below. Reflected infra-red might erroneously be reckoned as a part of the actinic light absorbed. Such a method would work well using for instance a mercury vapor lamp, with filter 86 of Gibson, Tyndall and McNicholas¹⁴⁴. The line at $366\text{ m}\mu$ ^{145b} is very strong and well isolated and would be transmitted almost free from contamination. On the other hand, the weak line at $302\text{ m}\mu$ could scarcely be separated effectively from the strong line at $313\text{ m}\mu$.

General Methods for Monochromatic Light. Low-voltage arcs deliver monochromatic resonance radiation of low intensity¹⁴⁹. That evoked in cold mercury vapor by transverse illumination from a mercury vapor lamp^{150, 151} is about one fortieth as intense in $\lambda 254\text{ m}\mu$ as the source¹⁵⁰, and has possibilities for practical work.

Ruled gratings are light-weak,¹⁵² but would be the only obvious expedient for monochromatic photochemistry in the Lyman region. A monochromator based upon Priest and Gibson's rotary dispersion colorimeter¹⁵³ is imaginable. Focal isolation, so successful in infra-red work¹⁵⁴ was used by Andrews^{15, p. 83} to separate visible from invisible and by Terenin¹⁵⁵ for different ultraviolet regions. Professor F. A. Saunders kindly tried out the method with the author, but spectrograms of the ultraviolet showed much false light over a range of $100\text{ m}\mu$.

¹⁴⁹ Cf. Foote and Meggers: Bur. Standards Bull., 16, 317 (1920).

¹⁵⁰ Wood: Physik. Z., 13, 353 (1912).

¹⁵¹ Cario and Franck: Z. Physik, 17, 205 (1923).

¹⁵² E. C. C. Baly: "Spectroscopy," 1, 157 (1924).

¹⁵³ Priest and Gibson: Bur. Standards Sci. Paper, 443 (1922).

¹⁵⁴ Rubens and Wood: Phil. Mag., 21, 249 (1911).

¹⁵⁵ Terenin: Z. Physik, 31, 33 (1925).

Monochromators employing refraction dispersion are at present relied upon for the best practicable compromises between intensity and monochromatic purity. Both improve with the size and optical refinements of the outfit.

The simplest type is a slit-shaped source at some distance from a prism, then a lens and a movable slit. In practice a collimating lens is added, as well as other optical parts. The beam is usually horizontal, but may be made vertical¹⁵⁶.

If a ready-made instrument is to be purchased, objectives less than 5 cm. in diameter are of limited usefulness in the case of weaker lines. The suggestion of Fabry¹⁵⁷ that any spectroscope plus an exit slit is a monochromator was hardly intended for photochemists.

A great variety of suitable prism monochromators has been described.

¹⁵⁶ Boll: Ann. Phys., 2, 5 (1914).

¹⁵⁷ Fabry: Rev. d'Optique, 1, 413, 445 (1922).

¹⁵⁸ Athanasiu: Rev. d'Optique, 4, 65 (1925).

¹⁵⁹ van Cittert: Rev. d'Optique, 2, 57 (1923); 5, 393 (1926).

¹⁶⁰ Beatty: J. Sci. Instr., 1, 33 (1923).

¹⁶¹ Feuss: Berlin-Steiglitz, catalogue.

¹⁶² Hilger: London, catalogue.

¹⁶³ Henri and Wurmser: Compt. rend., 157, 126 (1913).

¹⁶⁴ v. Halban and Siedentopf: Z. physik Chem., 100, 212 (1922).

¹⁶⁶ Houstoun: "Studies in Light Production," chapter 12, The Electrician Printing and Publishing Co., London.

¹⁶⁶ Kurtz: J. Opt. Soc. America, 13, 495, 1927 (1926).

¹⁶⁷ Leiss: Ann. Physik, 31, 488 (1925).

¹⁶⁸ Pfund: Phys. Rev., 7, 291 (1916).

¹⁶⁹ Rudberg: Z. Physik, 24, 257 (1924).

¹⁷⁰ Schoof: Z. Instrumentenkunde, 42, 82 (1922).

¹⁷¹ Wadsworth: Phil. Mag., (5) 38, 346 (1894).

"Home-made" Monochromators are relatively inexpensive, and if carefully constructed will prove very satisfactory. Dr. Villars of this laboratory has briefly described one⁶⁹ having a fused quartz prism $105 \times 105 \times 105 \times 80$ mm. Certain of the following suggestions were made by him or by Dr. P. A. Leighton of this laboratory. The above literature will suggest many variations.

The necessary rigidity may be had by using a slab of soapstone drilled for bolts or reinforced concrete poured around the various supports. Several front slits are provided, with increasing widths, and curvatures sufficient to neutralize distortion of the emerging beam at various wave-lengths^{171a}; the flat side of the bevel is toward the source. A constricted mercury vapor lamp can be bent so that its luminous column will have the average curvature of the slits. In this way vertical intensity gradients in the emergent beam are avoided. With most other light sources a quartz condensing lens of the type used in removing picture projectors can be used. Lenses figured to remove spherical aberration¹⁶² are preferable. Nickel or silicon¹⁷² spherical concave mirrors, though changing the spectral energy distribution of the source, have no chromatic aberration and can replace the lenses^{165, p. 103}. The rays should not be too far from perpendicular incidence. A fused quartz prism, 60° , and one of extra heavy flint $N_d = 1.69$ make an excellent outfit. Coblenz¹⁷³ has reported on the optical constants of lens and prism material. Fig. 1, kindly prepared by Mr. W. G. Leighton of this laboratory shows the distribution of wave lengths on the focal plane of a monochromator for four different materials. The high dispersion of water¹⁷⁴ from $250 \text{ m}\mu$ has suggested a hollow quartz water prism.¹⁷⁵ The lenses will usually be made of fused quartz. Striae can be seen between crossed nicols or by other methods¹⁷⁶. Combinations with fluorite or even water removes chromatic aberration. A prism table with lens taken from a small discarded spectroscope can be made over for larger units. A special table must carry the exit slit (of variable width) along the focal plane; it holds an exchangeable mounting for thermopile behind it, and another mounting for thermopile^{109, p. 154} still farther back. This last mounting can be moved across the light beam by a thread with millimeter pitch. Various automatic devices are suggested to keep the above system perpendicular to the light beam^{55, 168}. The parts are set up by trial, using a screen soaked in alcoholic anthracene^{11, p. 1256}. Collimation and minimum deviation at $\lambda_{366} \text{ m}\mu$ will usually suffice for other wave-lengths.

To set the exit slit squarely on a given line the position of maximum galvanometer deflection is found, or spectrograms of the emerging radiation^{4, p. 274} are made with an auxiliary spectrograph.

The emergent light may be made parallel or less divergent^{2, p. 221} by an additional lens. This greatly diminishes the light incident upon unit area of cell face, and cuts down percentage accuracy of thermopile readings. Also, a greater mass of reactant is needed to absorb a given amount of energy, which

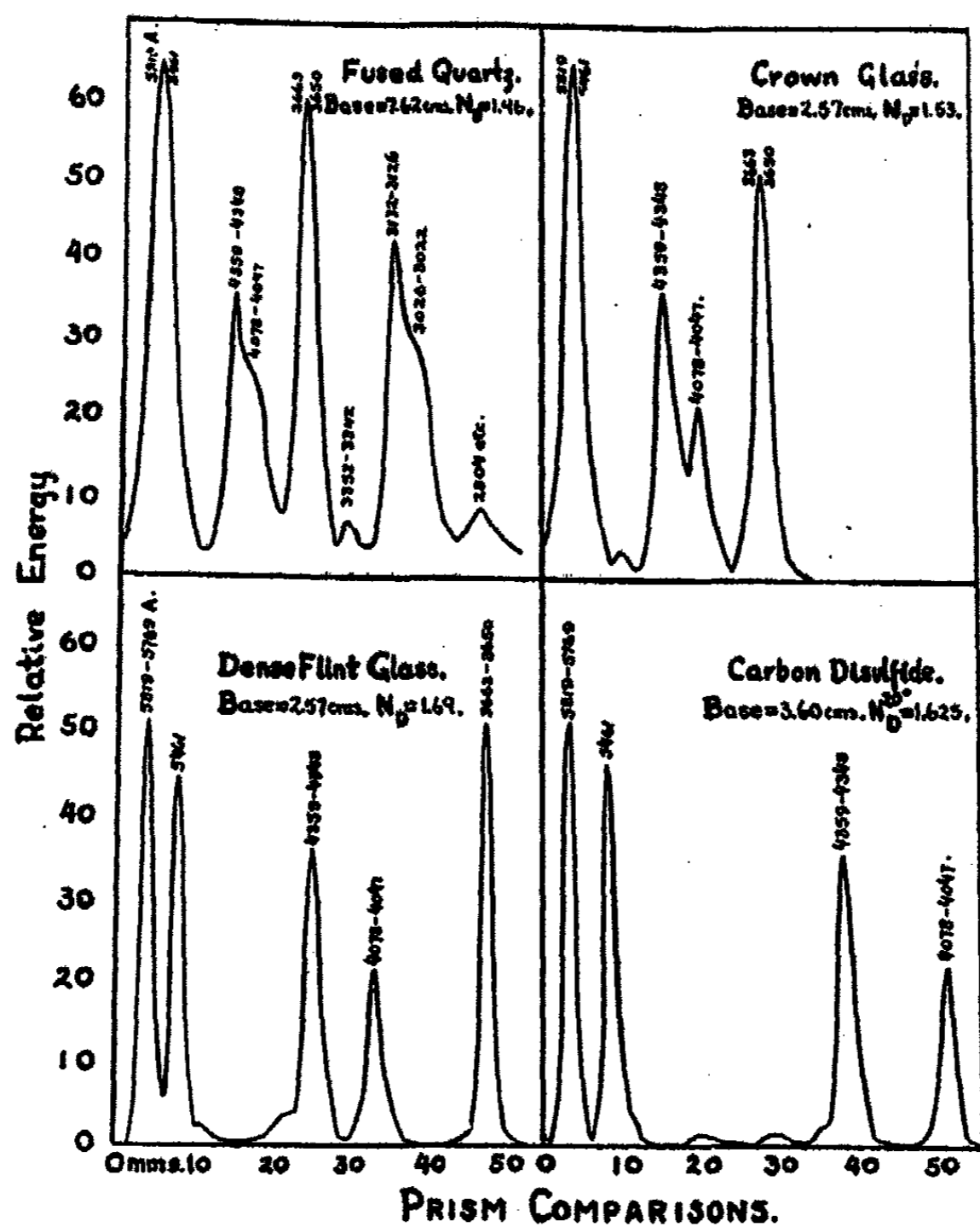


FIG. 1

magnifies analytical errors. To meet this difficulty Villars used a cell of trapezoidal cross-section placed close to the exit slit. The glass sides diverged at the same angle as the emergent beam of 366 $m\mu$. The front quartz window was only slightly wider than the exit slit used.

Instead of integrating the light with a surface bolometer^{1, p. 749} or thermopile, Villars⁵⁹ read his linear thermopile in about ten positions behind his cell, and made a graphical integral of intensity and area. He has shown mathematically¹⁷⁷ the propriety of measuring absorption coefficients in an analogous fashion. It is possible at least to halve the minimum error of 10% given by v. Halban^{164, p. 224} for absorption measurements by thermopile except for a

weak line near a much stronger one. The thermopile should cover the whole beam in a vertical direction, or else an integration vertically should be attempted.

Complications are introduced by fluorescence⁸⁶ p. 227 and by turbidity^{178, 179}. The method of Plotnikow¹⁴ p. 154 for continuous removal of precipitates is not intended for quantitative work. Changes in absorption may occur when gases⁵ p. 239 or solutes^{178, p. 321, 359; 178a} are mixed. Lambert's law should be proved to hold before assuming that the absorption coefficient varies with concentration. If two or more substances absorb light, this must be properly apportioned¹⁸⁰ between them, whether reactants or products, at each stage of the reaction. Water must be taken into account at the shorter wave-lengths, especially if the solute has small absorption; Kreuzler's figures¹⁸¹ are not based upon a unit layer. Warburg⁸ p. 1239 gives the proper corrections for reflected light; v. Halban and Ebert¹⁷⁸ describe a more refined correction for light absorbed and reflected by the vessel full of solvent. Absorption by good quartz is negligible to 250 m μ at least,¹⁸² but a small trace of iron tells a different story. The thermopile deflection at 254 m μ should not be decreased by more than 8 per cent by interposing a 1 cm. water cell. At 207 m μ absorption by quartz becomes perceptible^{4, 47}.

^{178a} Boll: "Recherches sur l'Évolution photochimique," 80 (1914).

¹⁷⁹ Hulbert: *Astrophys. J.*, 42, 205 (1915).

¹⁷⁸ Coblenz: *J. Optical Soc. America*, 4, 432 (1920).

¹⁷⁴ Duclaux and Jeantet: *J. Phys. Radium*, 5, 92 (1924).

¹⁷⁶ Duclaux: *Rev. d'Optique*, 2, 384 (1922).

¹⁷⁶ Smith, Bennett and Merritt: *Bur. Standards Sci. Paper*, 373 (1920).

¹⁷⁷ Villars: *J. Optical Soc. America*, 14, 29 (1927).

¹⁷⁸ v. Halban and Ebert: *Z. physik. Chem.*, 112, 335 (1924).

^{178a} v. Halban: *Z. physik. Chem.*, 120, 270 (1926).

¹⁷⁹ O. Warburg and Negelein: *Z. physik. Chem.*, 102, 241 (1922).

¹⁸⁰ Luther and Weigert: *Z. physik. Chem.*, 53, 408 (1905).

¹⁸¹ Kreuzler: *Ann. Physik*, 6, 421 (1901).

¹⁸² Joes: *Physik. Z.*, 25, 376 (1924).

False Light^{184; 18, pp. 203-7}. The purity of monochromatic light, $\lambda/\Delta\lambda$, may attain 10^6 in extreme cases,¹⁸⁷ but no such refinement is attempted in photochemical work. The degree of monochromatism which is necessary to attain a given degree of accuracy in a quantum yield will vary greatly with the system under consideration. If the photochemical efficiency ϕ reckoned in molecules per erg is practically constant over a given spectral region, the false light in the same region is equivalent to that of the principal wave-length. The error is worst for a weak line, near a strong line, in a region where $d\phi/d\lambda$ is large. Kuhn¹⁸⁶ required 2 to 2.5 quanta per molecule of ammonia over the interval 202.5 m μ to 214 m μ , but when a second prism was added and only the lines 206.3 m μ and 210 m μ were transmitted, no reaction at all could be directly observed. One may not agree with Kuhn's contention that the ammonia molecule must first absorb $h\nu$, and then $h\nu'$ not coinciding with any frequency absorbed by the normal ammonia molecule. But his findings should give pause to all those who work with imperfectly resolved light, especially when gases are involved.

Thermal radiators, especially, emit an amount of infra-red large in proportion to the light at shorter wave-lengths. Coblenz¹⁸⁸ has emphasized the importance of taking occasional thermopile readings behind a shutter of electric smoke or Corning red glass, and subtracting the indicated correction. False light in other spectral regions can be cut down by using a narrower monochromator slit, or a double monochromator^{189, 167} which squares (roughly) the fraction of the false light. If Lambert's law holds over a considerable range of thickness of layer of any given absorbent, the degree of monochromatism is probably good.^{178, p. 331} Filters used with monochromators cause a loss in intensity which magnifies the effect of analytical errors without necessarily making the monochromatism much better. Warburg^{6, p. 322} also Villars,⁹⁹ set up an auxiliary spectrograph with a narrow slit behind their exit slits, and examined the spectrogram for false light without attempting a quantitative correction. To make this, such a spectrogram could be taken after each photochemical experiment, measured up on a densitometer and relative intensities estimated at suitable intervals after some correction for change in photographic density with wave-length.⁹¹ The relative intensities could be more directly found by an auxiliary spectroradiometer. These would next be plotted for each position of the exit slit, on the same wave-length scale as that of the auxiliary spectrograph. The "pure light" would be arbitrarily marked off from the "false light," and the ratio between the two areas determined by graphical integration. The thermopile reading for the corresponding experiment would be accordingly corrected. Next the ordinates on the above curve would be multiplied by the uncorrected photochemical efficiencies found for the corresponding wave-lengths. Finally one would mark off the areas under the new curve corresponding to "pure light" and "false light," and deduct the latter from the total photochemical reaction, after correction for any dark reaction. A cruder method of correcting for false light, when using light filters, has been described by Luther and Forbes.¹⁸⁷

¹⁸⁴ Nutting: Bur. Standards Bull., 2, 439 (1906).

¹⁸⁵ Kuhn: J. Chim. phys., 23, 521 (1926).

¹⁸⁶ Coblenz: Bur. Standards Bull., 14, 229, 534 (1918).

¹⁸⁷ Luther and Forbes: J. Am. Chem. Soc., 31, 776 (1909).

Polarized Light. Ghosh states that circularly polarized light has a slightly greater photochemical action upon solutions than unpolarized light of equal intensity^{188, 189}. Weigert^{190, 191, 192} finds that polarized light produces changes in light absorption by certain solids.

Solids^{12, p. 738; 22, p. 224}. Methods for photochemical study of solids may be found from the references given. Plotnikow^{14, p. 144} formulates the progress of the reaction zone in gelatinized media where a colored reactant is decolorized by light without convection^{14, p. 144; 196}.

¹⁸⁸ Ghosh and Pukayestha: Chem. Abs., 20, 1953 (1926); ¹⁸⁹ Ghosh and Kappanna: 20, 3646 (1926).

¹⁹⁰ Weigert: Z. Elektrochem., 24, 222 (1918); ¹⁹¹ Z. Physik, 5, 410 (1921); ¹⁹² Z. physik. Chem., 101, 414 (1922).

¹⁹³ Padoa: Atti Accad. Lincei, 28 (2) 372 (1919).

¹⁹⁴ Noyes: Compt. rend., 176, 1468 (1923).

¹⁹⁵ Bowen and others: *J. Chem. Soc.*, 125, 1218 (1924).

¹⁹⁶ Benrath and Schaffgans: *Z. physik Chem.*, 103, 139 (1922).

Stirring. Warburg⁸, p. 1235 found that the speed of photolysis of potassium nitrate was the same whether the solution was stirred or not. In this case the absorption was not high, and the reaction was slow. On the other hand, stirring was indispensable when a mixture of maleic and fumaric acids⁹, p. 960 was irradiated because absorption was high and the speed of isomerization considerable. These principles are generally applicable. It would be superfluous to recount here all the types of stirrers for liquids, including gas bubbles. Warburg⁷, p. 300 shows how to keep a gas-stream well mixed while passing through a light-beam. If the stirrer is opaque to the radiation there must be corrections for its volume and for the shadow behind it. If transparent, one corrects only for the "hole" made in the reaction mixture, unless absorption is complete anyhow.

Temperature Regulation is now²¹, p. 346-8 believed to be less important than formerly,¹⁴ pp. 62-72 unless there is a considerable "dark reaction." The temperature coefficients of photochemical reactions proper seem to be small. Much ingenuity has, however, been expended on "light-thermostats," few of which would be suitable for monochromatic work. Running water,¹⁹⁷ water-cooled flasks,¹⁹⁸ liquid thermostat with glass walls,¹⁹⁹ stirrer of coiled tube through which chilled brine circulates,¹⁹⁷ airbath and fan, transparent vapor or liquid baths,²⁰⁰ envelope of refluxed naphthalene,²⁰¹ electric ovens^{200, 202, 203} are typical devices.

Plotnikow¹⁴: pp. 68-106; Plotnikow¹⁴: pp. 122-130; Jung¹¹: pp. 1504-5.

¹⁹⁷ Bolin: *Z. physik. Chem.*, 93, 721 (1919).

¹⁹⁸ Allmand: *J. Chem. Soc.*, 127, 822 (1925).

¹⁹⁹ Berthoud: *J. Chim. phys.*, 21, 308 (1924).

²⁰⁰ Weigert: *Ann. Physik*, 24, 55 (1905).

²⁰¹ Bodenstein and Lütkenmeyer: *Z. physik. Chem.*, 114, 208 (1924).

²⁰² Coehn and Becker: *Z. physik. Chem.*, 70, 93 (1910).

²⁰³ Kuhn: *Compt. rend.*, 178, 708 (1924).

Dark Reaction Velocity. This is determined inside or outside of the reaction vessel by the usual methods. If the dark reaction is important all work should be carried out at the lowest possible temperature, and the reaction layer should not absorb more than half of the incident light. Wegscheider¹²⁴ points out that the photochemical reaction is not the difference between total, and dark reaction determined separately. The error in such an assumption would be negligible, however, if total reaction is small in comparison with amount of reactant initially present. If the temperature is not constant during exposure to light, the temperature coefficient of the dark reaction may have to be measured, and the total dark reaction found by summation for a number of short time intervals.

Calculation of Results. Wegscheider¹²⁴ gives various equations for reaction velocities, and integrals, developed exclusively from the standpoint of dark reactions. He compares his deductions with those of Plotnikow,¹⁴ taking issue with him upon certain points¹⁸³. Warburg¹⁻⁹ was the first to make adequate calculations of quantum yields⁸⁹; he included all the important cor-

reactions except that for false light. Allmand's report²¹ summarizes recent conclusions based on observations of reaction velocities, while the Oxford symposium¹²⁵ is concerned primarily with quantum yields. These two methods of formulating photochemical reactions are supplementary,^{21, p. 344} and are interconvertible when complete quantitative data are available for monochromatic intensities, absorptions, concentrations and quantities transformed during given intervals. The less complete such data are, the more cautious must be any interpretation, and the more commodious the holes provided by the author for his own escape.

¹²⁵ Wegscheider: *Rec. Trav. chim.*, 44, 1118 (1925).

Analytical Methods are chosen with reference to their probable errors and with reference to the quantity of product which can be formed with the given light source in the time available. Time may be limited by a rapid dark reaction or by laboratory conditions. To form a millimol of product, for instance, with unit quantum yield at 366 m μ , 3.3×10^9 ergs must be absorbed. If the intensity is L ergs/sec and n the number of millimols needed, the time will be $n \times 9 \times 10^5/L$ hours (assuming complete absorption). A brand-new commercial mercury vapor lamp of standard type, run on 2.2 amperes and 10 volts/cm will deliver at an exit slit 40×1 mm, of a monochromator with 50 mm. objectives and an aperture ratio 4.5, 8×10^8 ergs/sec at 366 m μ , and 4×10^8 ergs/sec at 280 m μ where the quantum is nearly a third greater.⁶⁷ (Therefore the exposure times per millimol would be 110 and 3000 hours respectively.) The other important wave-lengths of the lamp have intensities between the two extremes. The time necessary to get n millimols would be increased by unfavorable quantum yields or by low absorptions. These considerations show why Boll¹⁶⁶ despaired of doing monochromatic work with a mercury vapor lamp if he had to determine the product by chemical analysis. Bodenstein and Lütkemeyer²⁰¹ used the full radiation of the tungsten arc to study hydrobromic acid formation "as dispersed or filtered light would have taken too long." Instances of this sort could be multiplied.

The constricted mercury vapor lamp without its maximum overload⁶⁷ will give ten times the slit illumination of the commercial lamp. Sparks from a 4 KW transformer^{108, p. 137} give and 2×10^4 ergs/sec at 207 m μ . It is difficult to increase monochromator intensities much beyond such values.

Chemical methods in such special cases as iodimetry^{2, p. 222} or electrometric titration¹⁶⁹ give with a small fraction of a millimol an accuracy of a few percent, which is the probable error of determining intensities. If a cylinder or bulb is fused to the top of the light reaction vessel the titration can be completed without transfer of the contents. Pregl's microchemical methods²⁰⁵ are suggestive to the photochemist. Gas analysis using chemical absorbents²⁰⁴ may suffice. Warburg^{3, p. 764} has stressed the importance of rapid removal and determination of unstable products, making correction for the fraction lost.

Certain physical methods^{11, p. 1492-6} of analysis require small amounts of substance. They are indispensable when chemical methods change the concentration of the substance to be determined or when a number of measurements must be made without heavy inroads upon the reaction mixture.

For gas reactions where the number of molecules changes one can use the quartz manometer with flattened tube,²⁰⁶ the quartz thread manometer,²⁰⁷ or the various manometers containing mercury^{1, p. 746} or other liquids. Hydrogen has been determined manometrically after condensing chlorine and hydrogen chloride in a side tube by adequate refrigeration.²⁰⁸ Such a method is particularly useful when the number of molecules does not change. Light absorption measurements,²⁰⁹ if feasible, are advantageous. For liquids also absorption measurements have been used.²¹⁰ Conductivity^{9, 156, 211} and potentiometry²¹⁰ are very sensitive. The fluorescence change in ultraviolet light²¹² has been suggested as a means of following concentration. Photoelectric effects have been employed^{213, 214}.

²⁰⁶ Bredig and Goldberger: *Z. physik. Chem.*, 110, 536 (1924).

²⁰⁷ Pregl-Fyleman: "Quantitative Organic Microanalysis." P. Blakiston's Son and Company, Philadelphia (1924).

²⁰⁸ Bodenstein and Kistiakowski: *Z. physik. Chem.*, 116, 371 (1925).

²⁰⁹ Haber and Kerschbaum: *Z. Elektrochem.*, 20, 296 (1914).

²¹⁰ Bodenstein and Dux: *Z. physik. Chem.*, 85, 300 (1913).

²¹¹ Pusch: *Z. Elektrochem.*, 24, 336 (1918).

²¹² Rideal and Norrish: *Proc. Roy. Soc.*, 103A, 357 (1923).

²¹³ Schwartz: *Ber.*, 58, 746 (1925).

²¹⁴ Mellet and Bischoff: *Compt. rend.*, 182, 1616 (1926).

²¹⁵ Volmer: *Ann. Physik*, 40, 775 (1913).

²¹⁶ Volmer and Riggert: *Z. physik. Chem.*, 100, 502 (1922).

Reaction Vessels. For quantitative work the faces should be plane, and perpendicular to the light beam. Warburg¹⁻⁹ developed in a high degree the cylindrical cell with plane parallel ends for liquids, and for gases in rest or in flow at pressures from 1 to 400 atmospheres. He used a lens behind the opening in the focal plane to make the rays parallel.^{2, p. 221} It was necessary to fill the cell with radiation when an unstable product such as ozone was flowing through it. The trapezoidal vessel for use in diverging light has been described above.

Crystal quartz must be cemented or clamped, but fused quartz cells cylindrical, rectangular or trapezoidal can now be made either in the oxyhydrogen flame or by applying in powdered form a flux slightly more fusible than the quartz and fusing the joints together all at the same time in an electric furnace. A new glass has recently been described by Hood¹⁴⁸ which would be serviceable down to 200 m μ , and which can be had in sheets several inches square. More information concerning its resistance to chemicals would be welcome. Other promising glasses are said to be in process of development. Cements^{12, p. 693; 235} should be avoided if possible, but they will give good service if intelligently selected. Warburg^{9, p. 960} ground his surfaces accurately and found that the thinnest film of paraffin, with a clamp, was sufficient. Fused silver chloride, used as described by Hulburt²¹⁵ makes good joints between quartz and glass, and graded seals are possible. Other cements that have been found useful are fish glue, gelatine and concentrated acetic acid, wax and colophonium, "piccin" (a German product), de Khotinsky, lead oxide and glycerine,²²⁵ lead borate and various dental cements.

Spherical vessels should in general be avoided, and cylindrical vessels illuminated perpendicular to their axis are unsuitable for quantitative work. Formulas for absorption in the latter^{14, p. 155} are not corrected for reflected light. Concentric annular vessels, one of which may be a mercury vapor lamp¹⁶ and another a light filter¹⁷ or a water cooler¹⁷ constitute very compact and efficient systems, especially for qualitative work, and make it possible¹⁸ to use the shorter ultraviolet, which is absorbed by air.

Among recent specimens of apparatus for investigation of gases include one of Coehn and Jung¹⁹, the whole of which could be heated to the softening point of glass to remove adsorbed gases, also one of Marshall^{19a} which could be baked in a furnace at 300° to 400° for the same purpose while passing electrolytic chlorine. Norrish and Rideal²⁰ devised a train for mixing hydrogen, chloride and oxygen in any proportions, dried with pentoxide, and measured manometrically. Porter, Bardwell and Lind²¹ realized a valid comparison of hydrogen-chlorine mixtures of equal sensitivity subjected to light and to radiochemical action.

¹⁶ Hulburt: *Science*, **56**, 147 (1922).

¹⁷ Fischer: *Physik. Z.*, **6**, 575 (1905).

¹⁷ Marshall: *J. Phys. Chem.*, **30**, 34 (1926).

¹⁸ Coehn and Stuckhardt: *Z. physik. Chem.*, **91**, 722 (1916).

¹⁹ Coehn and Jung: *Z. physik. Chem.*, **110**, 714 (1924).

^{19a} Marshall: *J. Phys. Chem.*, **30**, 757 (1926).

²⁰ Norrish and Rideal: *J. Chem. Soc.*, **127**, 787 (1925).

²¹ Porter, Bardwell and Lind: *J. Am. Chem. Soc.*, **48**, 2603 (1926).

Special Procedure with Gases. Intensive drying has been discussed at length in the literature^{21, pp. 349, 358; 11, pp. 1557-60; 222, 223}. The Budde effect has been unraveled by Lewis and Rideal.²⁴ Weigert and Kellermann²⁵ have devised a most ingenious apparatus for taking many photographs of the Draper effect during the initial 1/40 second of exposure. Coehn and Heymer²⁶ have followed the hydrogen-chlorine reaction in a jet from which the gases emerged into an atmosphere of hydrogen, to eliminate effects of contact with walls.

Of extreme importance in photochemical theory and practice are the reactions initiated by rayless collisions with excited atoms or molecules^{21, pp. 361-367; 226a}. Experimentation with excited mercury vapor has developed some special types of apparatus²⁷.

²² Tramm: *Z. physik. Chem.*, **105**, 356 (1923).

²³ Norrish: *Trans. Faraday Soc.*, **21**, 575 (1925).

²⁴ Lewis and Rideal: *J. Chem. Soc.*, 1926, 583, 596.

²⁵ Weigert and Kellermann: *Z. physik. Chem.*, **107**, 1, (1923).

²⁶ Coehn and Heymer: *Ber.*, **59B**, 1794 (1926).

^{26a} Franck and Jordan: "Anregung von Quantensprüngen durch Stöße." Berlin, Springer (1926).

²⁷ Franck and Cario; *Z. Physik*, **11**, 161 (1922); **17**, 202 (1923).

²⁸ Duffendack and Compton: *Phys. Rev.*, (2) **23**, 583 (1924).

²⁹ Noyes: *J. Am. Chem. Soc.*, **47**, 1003 (1925).

³⁰ Hirst: *Proc. Cambridge Phil. Soc.*, **23**, 162 (1926).

³¹ Taylor, Marshall and Bates: *Nature*, **117**, 267 (1926).

³² Rideal and Hirst: *Nature*, **117**, 449 (1926).

³³ Dickinson and Sherill: *Proc. Nat. Acad. Sci.*, **12**, 175 (1926).

³⁴ Neville: *J. Phys. Chem.*, **30**, 1181 (1926).

ABSORPTION COEFFICIENTS

BY HENRY G. DE LASZLO*

A great divergence of views¹ as to the exact mechanism of absorption in photo-chemical reactions still exists. We shall understand this mechanism better if research be undertaken on the absorption spectra of each of the several components of the reacting system, be it in solution, or in gaseous phase. These spectra should be measured quantitatively, i.e., the exact positions of the absorption bands in the spectrum and their absorption coefficients should be determined accurately before commencing a study of the reaction. This might give a clue as to why for a given reaction, light of one wave-length is photo-chemically active, and inactive if of another wave-length. Until very recently, absorption coefficients have only been determined for solutions or pure liquids. These will therefore be discussed first. The methods may be divided into two classes, A and B.

(A) In general, photographic methods are the best and nearly all of them depend on the following principles:

A common light-source, which is usually an iron spark, is optically divided into beams of equal intensity I . One (a) passes straight into the spectrograph and the other (b) reaches it after having traversed the solution. Now if by some means (a) can be varied equally throughout the spectrum with one of the methods cited below, or if the time of exposure t be changed for any given concentration one would be able to find some position (λ) common to the two spectra where the lines are of equal intensity. This is plotted against the corresponding absorption coefficient Σ .

The molecular absorption coefficient Σ is calculated from the relations $I = I_0 \cdot 10^{-\Sigma cd}$ where c is the molecular concentration and d the thickness of the solution or gaseous layer, I being the intensity of the light before entering the solution and I_0 the light after traversing same. Since I is proportional to t , the time of exposure for a given photographic effect, then $\Sigma = \frac{x c}{d} \cdot \log \frac{t}{t_0}$.

x is the constant for the photographic emulsion used, and lies between .8 and .9. Thus we see that either I or t may be varied.

There are a variety of ways of changing I and they may be roughly classed as follows:

- I. Varying distance of the light source.
- II. Diaphragm in path of rays.
- III. Absorbing medium.
- IV. Nicol prisms.

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¹ Trans. Faraday Society, 21, 438 (1926).

I. This is usually the most accurate and theoretically correct method, but it is difficult to carry out in practice. Schaefer has, however, developed it and the apparatus can be obtained from Zeiss-Jena.²

II. Sectors

An equipment for visual spectrophotometry has recently been adopted by Guild.³ This method uses a rotating sector with variable aperture and depends upon the validity of Talbot's Law as shown by Hyde.⁴ Many experiments have shown that the latter holds to within the accuracy of the best photometric measurements down to quite small angular apertures. The original sector photometer was introduced by Hilger in 1913, and has been mostly used in conjunction with quartz or glass spectrographs.⁵

An improved form of sector photometer was originated by Judd Lewis,⁶ but the apparatus is both expensive and difficult to keep in adjustment, though very rapid in use. When using the photographic method, it is best to use only two sets of exposures, and one aperture of the sector, at the same time varying the thickness of the solution layer. This sector method can be used throughout the visible and ultra-violet regions and gives very accurate curves.

Wire Screens

Winther⁷ describes the method of reducing I by means of blackened wire screens placed in the path of one of the beams. These screens are perfectly achromatic and any reduction of I can be obtained by varying the spacing and thickness of the wires. A set of screens can thus be made to cover any range of Σ .

III. Merton⁸ uses a sheet of quartz upon which a platinum wedge has been cathodically deposited. This is found to be entirely non-selective in its absorption and can be calibrated accordingly, and then placed in the path of one of the light beams.

IV. Most of the methods for investigating the visible spectrum are of this type. The König-Martens spectrophotometer enables Σ to be determined for each λ . It has been both universally applied and frequently described.⁹

A spectrophotometer has recently been constructed by Bellingham and Stanley.¹⁰ They use nicol prisms of special construction which are transparent down to the limit of calcite 2500 Å. It is attached straight onto the slit of a spectrograph and as in II employs the juxtaposition of two spectra. It is perhaps more accurate than the sector photometer owing to the difficulty of cutting sector openings accurately. Its shape, however, does not allow of having solution layers thicker than 5 cms.

² *Z. angew. Chem.*, 33, 25 (1920).

³ *Trans. Opt. Soc., London*, 26, 74 (1925).

⁴ *Bull. Bur. Standards*, 2, 1 (1906).

⁵ *Cat. of Adam-Hilger*, H-3 (1924).

⁶ *J. Chem. Soc.*, 115, 312 (1919).

⁷ *Z. wiss. Phot.*, 22, 125 (1923).

⁸ *Proc. Royal Soc.*, 97, 181 (1920).

⁹ *Ann. Physik*, (4) 12 984 (1903).

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A method whereby the light intensity is kept constant, and the time of exposure and concentration being varied, has been used for many years by Victor Henri.¹¹ Henri's photographic method is applicable over the whole range of 8000-2000 Å using a glass spectrograph for the visible, and a Hilger quartz E-2 instrument for the ultraviolet. It is simple and its accuracy has been rigorously tested.¹² The author has used it for many years, and the following refinements may prove useful. A light source of unvarying intensity is a prime necessity to insure accuracy. We use a 2 mm. spark between iron electrodes (8000-2500 Å) and copper for the range 2500-1900 Å, quenched by a synchronous rotating gap to prevent arcing and assure constancy. Solutions of known molecular concentration are made up in optically pure hexane,¹³ alcohol or ether. A Baly absorption tube constructed of fused quartz with the inner tube ground into the outer like a hypodermic syringe is then filled with the solution. A similar tube is filled with the pure solvent. The spark spectrum after having traversed a thickness d of the solution for a time t is photographed with the spectrograph using a slit height of 1-2 mm. After moving the plate carrier down a distance equal to the spectrum width a second exposure for time t_0 (5-10 seconds) is made through the same thickness d of solvent. A metol-hydroquinone developer is used. A Leitz-Metz¹⁴ binocular microscope with a magnification of 25 X may be employed without eye-strain for identifying the lines of equal intensity for each set of exposures in which d is constant. By varying t , d , and c , the Σ corresponding to any λ can be determined to $\pm/\text{Å}$ and is plotted against $1/\lambda$.

To supplement the above methods a continuous source of light should be passed through the solution in order to locate intensity maxima of the smaller absorption bands. A gas-filled tungsten^{15, 16} lamp is satisfactory down to 3000 Å, or a high frequency spark^{17, 18} under distilled water between duralumin or copper electrodes, using the iron spark as a standard, covers the whole spectrum down to 2000 Å.

(B) *Photoelectric Cell and Microphotometer Methods.* Direct reading methods consist in using a thermopile or photoelectric cell instead of the eye in conjunction with some form of constant deviation spectroscopy to act as a monochromator. Thus a direct measurement of light absorbed for each wavelength may be made by noting the galvanometer or electrometer deflection before and after traversing the absorbing medium. The most accurate work

¹¹ "Études de Photochimie."

¹² Henrich: "Theorien der organischen Chemie," 348 (1924); Ley and Volbert; Z. wiss. Phot., 23, 41 (1924).

¹³ Castille and Henri: "Bull. Soc. Chim. biol., 6, 299 (1924).

¹⁴ de Laszlo: Proc. Roy. Soc., 111, 363 (1926).

¹⁵ de Laszlo: Ind. Eng. Chem., 19, 1367 (1927).

¹⁶ U. S. P. 1, 501, 059 Leitz (Wetzlar).

¹⁷ Loebe and Ledig: Z. tech. Physik, 6, 325 (1925).

¹⁸ deLaszlo: J. Am. Chem. Soc., 50, 899 (1928).

¹⁹ Howe: Phys. Rev., (2) 8, 676 (1916).

²⁰ Strachan: Koken-Stähler, Vol. II, p. 519 (1919).

There are a number of other methods of Spectrophotometry in the visible region which are well described in the J. Opt. Soc. America, 10, 170 (1925), and in Bur. Bur. Standards, 18, No. 440 (1922); Weigert: Ber., 49, 1496, 1530 (1916); Jones: J. Opt. Soc. America, 10, 561 (1925).

has been that of Halban and his pupils,¹⁹ who extended their observations throughout the visible and ultra violet portions of the spectrum. Gibson²⁰ has developed a null method which seems promising, but until now has only been used for the visible region.

Photographic^{21, 22}. Here a constant beam of continuous light is passed through the solution onto a spectrograph for a known time. The same exposure is repeated without the solution, the spectrum being in juxtaposition to the former. This is followed by an iron comparison spark.

The absorption will be clearly seen on the continuous background and is measured in some form of direct reading microphotometer^{23, 24} using either nicol prisms or neutral tint glass wedges to obtain a matching of photographic density. Automatic registering^{25, 26} photometers are the most convenient. In all cases the instruments may be directly calibrated in Σ beforehand by means of some known substance.

The Determination of the Absorption Coefficients of Vapors and Gases has been much neglected until very recently. Considerable work has, however, been done by Henri and his pupils in measuring the exact position of absorption bands and their fine structure. For substances with high vapor²⁷ pressure at 70°C we use tubes of fused quartz into which, after evacuation, a small amount of the vapor is allowed to enter. By varying the pressure and passing continuous ultra-violet light through the tube for the same length of time t , we get a complete curve showing all fine structures with comparative data as to their absorption coefficients. The latter may be more accurately determined by methods similar to solution spectra using an iron spark. For substances with a very low vapor pressure at 20°C we use quartz tubes of a special design electrically heated throughout a wide range of temperatures. The exact values for Σ may be found by inserting weighed quantities of substance into an apparatus consisting of a number of quartz absorption tubes of known total volume and of varying lengths connected to a common reservoir. We then will know the number of gram-mols per litre and hence from the time of exposure and thickness of layer can calculate Σ for each λ .

The same system may be adapted for bodies with low V.P. by making the apparatus smaller and inserting all but the reservoir in a furnace which is heated to the highest temperature to be used in the experiment. The reservoir is heated in a separate furnace whose temperature can be accurately measured and may be raised in steps, photographs being taken at each step through each of the several tubes. Such a series of photographs will again give us exact data as to both Σ and the position of the bands.

¹⁹ Halban and Siedentopf: *Z. physik. Chem.*, 103, 71 (1922); Halban and Eisenbrand: *Proc. Roy. Soc.*, 116, 153 (1927).

²⁰ Bull. Bur. Standards, No. 349, 327 (1919).

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THE EXCITED SYSTEMS FORMED BY THE ABSORPTION OF LIGHT

BY LOUIS A. TURNER

The law of Photochemistry which has been known the longest and is the best-established and the most fundamental, is that of Grotthuss and Draper, viz., that the only radiation which will produce a photochemical reaction is that which is absorbed by the reacting system. The process of absorption is, therefore, of primary importance and any generalization concerning this process should be of some importance for the photochemist. Some of the newer developments of the theories of atomic and molecular spectra and their relations to the structure of atoms and molecules are concerned with the various possible processes of the absorption of light and the properties of the excited systems produced by that absorption. This article will be devoted to a brief discussion of such of these results as may have some bearing on photochemical reactions.

The two principal postulates of Bohr's theory of atomic and molecular structure which has been so successful in correlating the spectroscopic phenomena are:—1) A molecular system can exist only in certain stationary states having definite energies and 2), when the system changes from one of these stationary states of greater energy to another of lesser energy monochromatic radiation is emitted, its frequency being given by the relation $h\nu = E_1 - E_2$. ν is the frequency, h is Planck's constant ($= 6.55 \times 10^{-27}$ erg sec.), E_1 and E_2 are the energies of the molecule in the two states, respectively. The absorption of light is the reverse process, producing a change from a stationary state of lower energy to one of higher energy.

A single atom is believed to be made up of one minute, massive, positive nucleus and numerous electrons so that the different stationary states must correspond to different configurations of the electrons. A discussion of the quantum rules according to which these stationary states are determined is beyond the purpose of this article. Each line of an emission spectrum, therefore, is produced by one of the many possible changes of the atom from a higher to a lower stationary state. Likewise, the absorption lines correspond to changes from states of low energy to ones of higher energy. The absorption line spectrum is, however, always much simpler than the emission line spectrum because at ordinary temperatures the vast preponderance of the atoms exists only in the stationary state of lowest energy, the normal state, and consequently can absorb light of only those frequencies which correspond to transitions from that state to those of higher energy.

The atom which has absorbed light now has a different electronic configuration and is, from one point of view, a new chemical substance, of high energy constant. If the light absorbed is in the visible region, the energy per excited atom is 2 or 3 volts, roughly equivalent to 50,000-75,000 gram calories

per gram mol (one volt of energy is the kinetic energy of an electron which has fallen through a potential drop of one volt. One volt per atom equals 23.0 kg. cal. per gm. mol.) The atom in this excited state may do one of several things. It may simply reradiate light of the frequency of that absorbed, it may radiate light of a lower frequency by a transition to an intermediate state, or it may give up its energy without radiating upon collision with another atom or molecule. It has been found by a variety of methods that an atom remains in one of these excited states into which it is put by absorption of radiation an average time of the order of 10^{-8} seconds.¹ If the excited atom is in a rarefied gas it will reradiate its energy before making a collision, so that such gases usually show some sort of a fluorescence spectrum. There are, however, for some atoms, a few stationary states in which the atom can remain an indefinitely long time without radiating any of its energy of excitation. This happens when there is a stationary state of greater energy than the normal one, but of such a sort that there is no possible transition from it to a lower state with the emission of radiation, or *vice-versa*. For instance, the excited state of a mercury atom of lowest energy which can be reached by the absorption of light is the 2^3P_1 state ($2P_2$ in the old notation) into which the atom is changed by absorption of light of a wave-length of 2537 Å. U. A small fraction of a volt below this is the 2^3P_0 state from which the atom can change to various higher states by the absorption of radiation; but, once in it, can not revert to the normal state by radiating, neither can it be brought to this state from the normal one by the absorption of radiation. In this and other such cases, these so-called metastable states can be reached, however, by transitions from states of still higher energy. It has been shown by Dorgelo² that in pure neon at low temperatures atoms will remain in 16.6 volt excited stationary states for at least $1/10$ of a second, as indicated by the absorption of light by atoms in these excited states. A slight trace of impurity cuts this life down to a time too small to measure.

This disappearance of the metastable excited atoms and the quenching of the fluorescence of a gas with increasing pressure or admixture of other gases show that the excited atoms can lose their energy by some other method, presumably upon collision with other atoms or molecules. Such processes were called "collisions of the second kind" by Klein and Rosseland³ who predicted them by a theoretical argument. They showed that if, when two atoms collide, part of their kinetic energy can be used to raise one of the atoms to an excited stationary state (a "collision of the first kind") the reverse process must also be a possible one. Various sorts of collisions of the second kind were experimentally investigated by Cario and Franck⁴ who showed that Hg atoms excited by the absorption of light of a wave-length of 2537 Å. U. can excite other atoms such as Tl and Na, which will emit their own spectrum, the excess energy appearing as kinetic energy. They also showed that the excited Hg atoms will produce a chemically activated form of hydrogen, presumably atomic hydrogen. All of the energy of excitation is not necessarily used up in the process occurring at the first collision. The atom may first be put into a metastable state, giving up a small amount of energy, and then remain there

until it finally makes a collision in a way favorable for it to give up all of its energy of excitation. Experiments of Donat⁵ and of Wood⁶ indicate that this is what happens to excited Hg atoms in mixtures with argon or nitrogen at pressures of the order of one-tenth to one atmosphere. Processes of this kind must be involved in the various photochemical reactions⁷ produced by illuminating mixtures of Hg vapor and other gases with 2537 light, many of which have been studied since Cario and Franck's original experiment. This type of photochemical reactions is, of course, a very special one for it is light of only an exceedingly narrow region of the spectrum which has any effect upon the mixture, viz., the very center of the 2537 line. Self reversal of this line removes all of the effective radiation if the mercury arc lamp used for a source is not sufficiently cooled.

Stuart⁸ has made a study of the quenching of the resonance fluorescence of Hg vapor produced by the admixture of various other gases. Different gases give vastly different quenching effects showing that the probability of a radiationless transfer of energy at collision depends upon the nature of the colliding molecules. It is of interest that the effectiveness of this quenching is so great for some gases that even if it is assumed that the probability of occurrence of a radiationless transition at collision is unity, it is necessary to ascribe a much larger effective radius to the excited Hg atom than the radius of the normal Hg atom as deduced in other ways. Similar experiments have been performed with Na vapor by Mannkopf⁹, who finds a different relative order of effectiveness for the different gases from that found by Stuart for Hg vapor.

In many cases the absorption lines can be arranged in series converging to a limit on the side of shorter wave-lengths. Beyond this limit there is a region of continuous absorption. The successive lines of a series, by Bohr's theory, have to do with transitions from the normal state to a set of states of higher energy, one electron becoming less and less tightly bound to the nucleus. The limit corresponds to complete removal of this electron, i.e., ionization. The region of continuous absorption beyond the limit corresponds to ionization of the atom and ejection of the electron with various amounts of kinetic energy, continuous because that kinetic energy can have any value. Such absorption by Na and K has been investigated by Harrison¹⁰ and the predicted photo-ionization has been studied by various workers.¹¹ The continuous absorption of X-rays is a similar phenomenon. Experiments with X-rays have shown¹² that the electrons have the expected velocity given by the equation

$$\frac{1}{2} m v^2 = h\nu - P$$

The spectra of molecules, both emission and absorption, are interpreted in the same way as those of atoms. The differences between them are to be attributed to the more complicated structure and resulting increase of the number of degrees of freedom of the molecules. For the molecules, as for the atoms, there are various electronic configurations but instead of each of these giving a single stationary state it is split up into a two-fold multiplicity because of the various possible energies of mutual vibration of the different nuclei of the molecule and the various possible energies of rotation of the molecule as a whole. All of these motions are quantized so that for a given

set of electron quantum numbers there are many possible vibration states and for each of these many rotation states. The number of stationary states of a molecule is therefore very great compared to that of an atom and the number of spectrum lines connected with transitions is correspondingly increased, giving rise to the complicated band spectra. For a complete treatment of this subject the reader is referred to the Bulletin of the National Research Council, No. 57, "Molecular Spectra in Gases."

This complication of the stationary states admits the possibility of transitions not possible for atoms. There are the rotation bands in the far infra-red region of the spectrum corresponding to changes of only the rotation of the molecule, and the vibration-rotation bands in the near infra-red corresponding to simultaneous changes of the vibration and rotation. The electronic bands are those which involve a change in the electronic quantum numbers and, therefore, correspond to a single line of an atomic spectrum but because of the complication of all the various possible simultaneous changes of the vibration and rotation the single line becomes a whole system of bands.

The excited molecule can, like the atom, reradiate part or all of its added energy to give a fluorescence spectrum. Such are the resonance spectra of I_2 , Na_2 , etc., studied by R. W. Wood¹³ and others. Collisions of the second kind presumably can occur and must be of great importance in the mechanism of photochemical reaction in which the absorbing substance is molecular, the exciting light being in the spectrum region of discontinuous band absorption. There is one possible type of collision which results in the dissociation of the excited molecule itself into component parts—a sort of auto-collision of the second kind. The energy of excitation of many molecules is considerably greater than the energy for dissociation and it seems quite probable that upon collision this excited molecule can give up its energy by dissociating itself. There is no very direct evidence for the occurrence of this process. Nor is much known about possible, molecular, metastable, excited, electronic states. There is evidence, however, that many electronic transitions of kinds which do not take place in atoms do occur in molecules so that the probability of the existence of these metastable excited states is much less.

Various band spectra have been analyzed and the electronic transitions discovered. In one case, that of the He_2 bands, there has been found a sequence of transitions converging to a limit according to the same law as do the lines of a series, and apparently for the same reason. Theoretically, at least, one might expect to be able to follow many such sequences to the limit of convergence and find a region of continuous absorption connected with ionization of the molecule. Such an absorption has not been found.

There are, however, regions of continuous absorption in the spectra of molecules which seem to be connected, not with ionization, but with dissociation of the absorbing molecules. They are continuous because of the continuity of the possible kinetic energies of the separated atoms. It is found that the energies of the excited states having the same electron quantum numbers are greater the greater the vibration quantum numbers, as one would expect, but that with increasing vibration quantum number the energy differ-

ences between these states become steadily less. (It is implied that molecules having zero rotational energy are being compared). The energies of these successive states can in several cases be represented by a very simple formula involving the vibration quantum number. It indicates that the energy difference between successive vibration states becomes zero for a finite vibration quantum number and a certain value of the energy. This is thought to be the energy at which the molecule dissociates into atoms. According to the quantum theory of the anharmonic oscillator the energy difference between successive vibration states is proportional to the frequency of vibration so that when this difference becomes zero so does the frequency, indicating that the binding force has become zero.

As an example, consider the absorption spectrum of iodine. Cold iodine vapor has a discontinuous band absorption in the red to green parts of the visible spectrum which merges into a region of continuous absorption beginning at about 4995 Å. U. and extending into the violet. The bands have been analyzed and are apparently connected with transitions from the single normal vibration state (actually multiple because of the various rotational energies) to various vibration states of one excited electronic configuration. The frequencies of these bands are related by a simple law which indicates that the frequency difference between them becomes zero at 4995 Å. U., the result of the convergence of these upper vibration levels. Dymond¹⁴ found that if iodine absorbed light of wave-length longer than this it would fluoresce but that if it absorbed light of a shorter wave-length in the region of continuous absorption there would be no fluorescence. In the first case the molecules were simply excited and could reradiate their energy but in the second case they were apparently actually dissociated.

Absorption of light of a wave-length of 4995 Å. U. will, therefore, produce dissociation of the molecule into two separate atoms having zero kinetic energy. The energy is 2.469 volts (volts $\times \lambda$ in Å. U. = 12345), whereas the experimental value for the heat of dissociation of I_2 is only 1.5 volts. The difference of 1.0 volts must be an energy of electronic excitation of at least one of the two atoms. Such an electronic energy would be expected since this optical dissociation is continuously connected with the band absorption which does involve an electronic change. On the other hand, when dissociation occurs the electronic energy must be that of one of the excited states of the atom. The spectrum of the iodine atom has not been analyzed, but, theoretically, there should be a low state near the normal one, the two forming a doublet P state. A recurring doublet difference between the frequencies of some of the strong lines of I in the Schumann region has been found.¹⁵ It presumably gives the energy of this next to the lowest state, the value being 0.937 volts. Subtracting this from the 2.469 volts energy for optical dissociation gives 1.532 volts as the heat of dissociation of iodine. This value is equivalent to 35.2 kg. cal. per mol. which is in satisfactory agreement with the direct experimental value of 34.5 kg. cal. per mol. Granting the theoretical interpretation of the spectra, the optical value is the more accurate. Kuhn¹⁶ has made

a similar study of Br_2 and Cl_2 and finds the same sort of relationships. The results are summarized in Table I.

TABLE I

| | λ of convergence | $h\nu_0$ | $2^3P_1 - 2^3P_1$ | D (spectroscopic) | | D (thermal) |
|----|-----------------------------|----------|-------------------|-------------------|--------|-------------|
| | | | | volts | kg cal | |
| I | 4995 | 2.469V. | 0.937 | 1.532 | 35.2 | 34.5 |
| Br | 5107 | 2.415 | 0.454 | 1.961 | 45.2 | 46.2 |
| Cl | 4785 | 2.577 | 0.109 | 2.468 | 56.9 | 57 |

One would expect that every set of vibration levels would converge in this way, the different sets being connected with different electronic states of the molecule and of the separated atoms. For substances of which the band spectra have been sufficiently analyzed and for which the various atomic states are known, it should be possible to get several independent determinations of this energy of dissociation. This has been done for one substance, hydrogen. Witmer,¹⁷ from the set of vibration states of which the normal state is the lowest found a heat of dissociation of 4.34 ± 0.01 volts. Dieke and Hopfield¹⁸ found in the far ultra-violet region of the spectrum a set of absorption bands and a region of continuous absorption as in iodine, continuous absorption beginning at 849.4 \AA . U. This limit gives 14.53 volts for the energy of dissociation of the H_2 molecule into one normal and one excited H atom. Assuming the energy of excitation of the H atom to be that of the state next above the normal, 10.15 volts, a value of 4.38 volts is obtained for the energy of dissociation. This agrees well enough with Witmer's value of 4.34 volts which involved a considerable extrapolation. 4.38 volts is equivalent to 100,900 kg. cal. per mol., in satisfactory agreement with the best direct experimental values. These ideas have been extended and applied to various other molecules by Birge and Sponer.¹⁹ The whole matter is discussed at length in Professor Birge's chapter in the report on molecular spectra in gases, referred to above.

Although it should be possible to apply these calculations in all cases, given a sufficiently complete analysis of a band spectrum, it does not necessarily follow that in all cases it is possible that normal molecules can be made to dissociate by the absorption of radiation, as the halogen molecules apparently actually do. The occurrence of such a dissociation means that there is a great probability of a large change of the vibration quantum number accompanying the electronic change. Franck²⁰ has pointed out that there is a connection between the change of the moment of inertia of the molecule in a transition and the magnitude of the most probable change of the vibration quantum number. The moments of inertia can be calculated from the energy differences between successive rotation states. In the spectra of substances like iodine, the moment of inertia of which is increased with the change to the higher electronic state, large changes of the vibration quantum number are the most probable, whereas in the spectrum of nitrogen of which the moment of inertia changes by a small amount, the most probable changes of the vi-

bration quantum number are the small ones. The increase of the moment of inertia means a corresponding increase of the separation between the nuclei in their position for equilibrium. It seems as if the electron configuration were changed from the normal one to the higher one instantaneously, leaving the nuclei practically the same distance apart. If this distance is then much less than the equilibrium distance for this excited state the molecule finds itself highly compressed and, being free to vibrate, does so with large amplitude. It may be that the energy of compression is greater than the energy necessary for complete separation of atoms when the nuclei are at rest in the equilibrium position. In this case the compressed molecule will expand, the nuclei passing through the equilibrium position with sufficient energy to separate completely with some kinetic energy left over. Whether this be the explanation or not, there is, nevertheless, the connection between a high probability of large change of the vibration quantum number and large change of the moment of inertia. The various other possible cases are discussed by Franck. Kuhn¹⁶ points out that I_2 , Br_2 and Cl_2 have, in the order given, a progressively greater weakening of the binding upon absorption as measured by the energy difference between successive vibration levels. The maximum adsorption by I_2 occurs just at the edge of the continuous region, that for Br_2 further into the continuous region, and that for Cl_2 well into it. There is, then, this sort of independent evidence for the primary optical dissociation of these halogen molecules by the absorption of light, which has often been postulated in the explanation of various photochemical reactions.

There is another type of process which may be of importance in photochemical reactions. It seems probable that in some cases a molecule in a quantized state may, instead of undergoing a transition to a lower state of high vibrational energy, change to a state where the atoms are completely separated, the remaining energy being radiated. A continuous emission spectrum would result in cases where this sort of process could occur. Blackett and Franck²¹ have advanced this as the best explanation for a certain continuous emission spectrum of H_2 which their experiments show to be the result of primary processes, i.e., independent of collisions with other molecules. Born and Franck²² have suggested the converse process to explain certain continuous absorption spectra such as the absorption by Hg vapor at high pressure on the long wave-length side of the 2537 line. Two atoms colliding with large kinetic energy form a temporary "quasi-molecule" which can absorb light to produce a definite quantized excited molecule, part of the energy being the kinetic energy of the colliding atoms, the rest being made up by the radiation. Such absorption may be of importance in photochemical reactions between gases at ordinary pressures.

The effectiveness of these atoms resulting from the dissociation of the molecule must depend to a certain extent upon the fact that in some cases they do not readily recombine to form molecules. This is in accord with Bohr's Correspondence Principle, in the case of highly symmetrical molecules such as I_2 or H_2 . Such highly symmetrical molecules when vibrating in the normal electronic state presumably have no vibrating electric moment. Classically,

they would neither emit nor absorb radiation so that the corresponding quantum radiation, the vibration-rotation bands, are missing. Such molecules can not be dissociated by absorption of radiation unless an electronic transition occurs so that the two atoms will not recombine with emission of radiation if both are in the normal state. Thus they do not combine except when there is some other body to take up the extra energy, as in a three body collision, or at the surface of a solid.

Practically all of the important theoretical and experimental work on band spectra has been done with diatomic molecules. Even they are sometimes rather hopelessly complicated so that it is not surprising that not much progress has been made in the study of spectra of still more complex molecules. There is no reason to doubt, however, that these more complicated molecules will behave in an analogous way.

In view of these various possible effects of the absorption of light it is no great wonder that Einstein's photochemical law is not accurately fulfilled by many reactions. Undoubtedly the primary process does follow the law, there being one excited system produced for each quantum absorbed, but even granting that none of the absorbed energy is re-emitted as fluorescent light, the subsequent course of the reaction will depend entirely upon the chemical properties of that excited system which may combine to give a small number of resultant molecules, or initiate a chain reaction, or act as a catalyst. The light merely serves to introduce an impurity, often of high energy content, into the system and the subsequent course of the reaction may be of almost any of the known types. The number of resultant molecules produced per quantum of light absorbed is, of course, an indication of the nature of the reaction subsequent to the absorption.

Since this article was written there have appeared numerous papers dealing with matters related to those discussed here. That NaI molecules are dissociated by the absorption of light of wave-length less than 2450\AA into normal I atoms and excited Na atoms, which then emit the P lines, has been shown by the experiments of Terenin,²³ of Kondratjew,²⁴ and of Hogness and Franck.²⁵ Franck, Kuhn and Rollefson²⁶ and Franck and Kuhn²⁷ have studied the absorption spectra of various alkali and silver halides. They discuss the theory of the optical dissociation of such heteropolar molecules and of the hydrogen halides, the absorption by which had been previously investigated by Tinge and Gerke,²⁸ and Bonhoeffer and Steiner.²⁹ That exceedingly dry chlorine has the same absorption spectrum as moist chlorine has been found by Kistiakowsky,³⁰ and by Kornfeld and Steiner,³¹ thus showing that the great influence of H₂O vapor upon the photochemical combination of H₂ and Cl₂ is one upon the reactions following the primary absorption. The author³² has recently found that iodine vapor illuminated by strong light from a carbon arc absorbs the light of the 1830.4 line of the iodine atom more strongly than when not so illuminated. This light should be absorbed by normal iodine atoms, so the experiment is taken to indicate the presence of the iodine atoms resulting from the optical dissociation.

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QUANTUM PROCESSES IN PHOTOCHEMISTRY

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The modern theory of absorption and emission of radiation by quanta is at once both an amplification and limitation of the fundamental law of photochemistry formulated by Grotthuss and restated in its application to the hydrogen-chlorine reaction by Draper. According to this law only light which is absorbed by a chemical system is active in producing chemical change. Quantum theory amplifies this law by defining more particularly the absorption act. The progress which has been made in this definition is indicated in a preceding communication of this series by Turner.¹ In so far as the quantum theory of absorption sets a limit to the energy available in a single absorption act it also sets a limit to the nature of chemical change that can result from such absorption. Thus, for example, if the absorbing system be composed of a single type of diatomic molecules and the light energy absorbed per quantum is less than the energy of dissociation of such molecules, it follows that such dissociation cannot occur as the result of absorption of a single quantum. Whether such dissociation may occur when the energy of a quantum exceeds the dissociation energy has already been discussed in some of its bearings by Turner. The relationship laid down by quantum theory between the energy of a quantum and the frequency of the radiation absorbed is given by the equation

$$Q = N h \nu \quad (1)$$

where Q is expressed in calories per mol, N is the Avogadro constant ($= 6.06 \times 10^{23}$), h is the Planck constant ($= 6.554 \times 10^{-27}$), ν is the frequency ($= c/\lambda$ where c is the velocity of light and λ its wave length and equals $1.048 \times 10^{10}Q$).

During the past two decades, largely as a result of ideas first put forward by Stark² and made definite by Einstein,³ the relationship between absorbed light energy and chemical reaction produced has been intensively studied. The attempt has been made to show that a simple numerical relationship exists between the number of absorbed quanta and the number of molecules brought to reaction as a result of the light absorption. In the most definite form, sometimes known as the Einstein Law of the Photochemical Equivalent, an exact equivalence between absorbed quanta and reacting molecules was postulated. Abundant evidence is now available to show that this exact equivalence only holds in very exceptional circumstances and that, in the majority of photo-chemical reactions, the relationship obtained deviates from equivalence to an extent characteristic of the system in question. The deviation may be in both directions. Many systems show manifold fewer reacting molecules than absorbed quanta. At the other extreme are reactions in which an enormous number of molecules react for every absorbed quantum. It might therefore be asked what advantage there could be in retaining the con-

cept of a relationship between quanta and reacting molecules. *It is the aim of the present article to set forth considerations which bear upon this problem.

The Analogy between Electrochemical and Photochemical Processes. Since the time of Grotthuss, and especially in recent times by Bancroft⁴ and by Baur,⁵ an analogy between electrochemical and photochemical processes has been stressed. The modern theory of quanta applied to photochemical systems is very much more definite than any such process of analogy. For the idea that the action of light is analogous to that of a voltaic cell or that 'photolysis is a molecular electrolysis,' quantum theory substitutes a perfectly definite statement as to the actual stages in the whole process. It postulates that the absorbing constituent of the system is changed by absorption of light, from its normal energy state in the dark, to an energy-rich form, the magnitude of the energy increase per unit absorbent, atom or molecule, being exactly that of the quantum, $h\nu$, of absorbed radiation. When the absorbing system is atomic, the nature of the energy change can be stated in terms of the quantum theory of atomic structure. Thus, in the case of mercury, the absorption of light of wave length $\lambda = 2536.7 \text{ \AA}$, is accompanied by the passage of the atom from the normal atom state (1S) to the excited state known as the 2^3P_1 state. The energy associated with this change is given by Equation (1) as equivalent to 112000 calories per gram atom of mercury in the excited state. When the absorbing system is polyatomic the energy absorbed is not necessarily wholly associated with an electronic change, but may also be distributed between the vibrational and rotational degrees of freedom of the absorbent. The total increase of all such types of energy is, however, given by Equation 1.

The quantum theory of photochemical processes, therefore, accounts for the existence of photochemical reactions by the presence in the reaction system of an energy-rich species and also of species with which such energy-rich atoms or molecules may react. The nature of the chemical change brought about by the agency of the light will depend on the normal chemical reactivity of the system and on the available energy. It is thus possible for all such chemical reactions as occur in the dark to occur with one of the constituents activated by light. It is, however, possible that reactions may occur in the light, which occur only to a negligible extent in the dark, by reason of the larger units of activating energy involved. Thus, the chance that a molecule in a system at temperature T shall possess, thermally, a quantity of energy equal to 100,000 calories is given by the Boltzmann relationship

$$e^{-100000/RT}$$

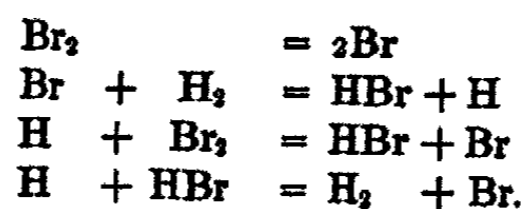
which, for the ordinary temperature range, is very small. Molecules possessing such energy units are created every time a quantum of light of wave length approximately 2800 \AA is absorbed.

Depolarizers.—In stressing the analogy between photochemical and electrochemical processes Grotthuss and others have referred to the non-absorbing components of a photochemical system as depolarisers, and thus associated them with the electrochemical depolarisers which take part in electrode reactions on the discharge of ions. The quantum concept of photochemistry

applied to such components sees in them merely reacting constituents of the system which may or may not partake in the reaction process depending on the energy quantities available. In electrochemical systems the reactions are mainly oxidation and reduction since they are generally processes involving electron transfers. In photochemical systems not only do oxidation and reduction occur but every other type of chemical process is possible, halogenation, hydration, hydrolysis, polymerisation or condensation, depolymerisation. In general, the photo-reaction will not be associable with a transfer of electrons but will be associated with the definite utilisation of activating energy.

The approach to an examination of this energy utilisation may be made through consideration of thermal reactions. If we heat up a vessel containing hydrogen gas, there will be negligible chemical change in the system until extremely high temperatures are reached. That is because the chemical reaction which can occur in such a system is the dissociation of molecules into atoms.^(a) Now, in order to dissociate, a molecule must receive as activating energy at least the dissociation energy of 100,000 calories and this, as the Boltzmann expression above shows, is a seldom occurrence. Marked concentrations of atomic hydrogen are only obtained thermally above 2000°C. If, however, we introduce into the hydrogen gas some other reacting gas, reaction may occur long before such temperatures are reached. Thus, with iodine, reaction occurs at a few hundred degrees of temperature since, as is now known,⁶ the activating energy demanded of such a system is that the colliding molecules of hydrogen and iodine shall *jointly* possess some 40,000 calories. The iodine may be regarded as a thermal depolariser of the hydrogen. In the reverse reaction, the dissociation of hydrogen iodide, the substance may be thought of as its own depolariser. If unimolecularly dissociated, an activating energy not less than 68,000 calories (the dissociation energy) is required, whereas in the 'depolarized process,' the bimolecular reaction, only some 44,000 calories of activating energy are required by a colliding *pair* of molecules.⁶

Bromine acts in an entirely different manner as a 'depolariser' of hydrogen. On the basis of the experimental data of Bodenstein and Lind,⁷ Christiansen,⁸ Polanyi⁹ and Herzfeld¹⁰ all independently showed that bromine atoms were the immediate agents of 'depolarisation' as is indicated by the reaction scheme:



Oxygen is actually an extremely poor 'depolariser' for hydrogen gas. There is no experimental evidence that the homogeneous thermal gas reaction occurs to any reasonable extent when studied in closed systems.⁶ The bulk of the reaction is confined to the walls of the containing vessel.

^(a) Excluding the possible formation of polymers H₂, H₄, etc.

This varying reactivity of systems under the influence of thermal activation is exactly paralleled by photochemical systems. As recorded by Bancroft in a following paper, copper sulphate solutions are stable of themselves in light, but are readily reducible when white phosphorus is present in the system. Potassium permanganate solutions show a certain degree of instability under suitable illumination but this instability is enormously increased by the addition of sodium oxalate.¹¹ There does not, however, appear to be any essential point of difference between this and the thermal hydrogen and hydrogen-iodine systems just discussed. What is plain is that the reactivity of normal thermal systems of potassium permanganate and sodium oxalate is less frequent than the reactivity of photochemically activated permanganate with sodium oxalate. Such systems are, however, quite complex and it is desirable first to exemplify the quantum concept of photochemical reaction with much simpler systems, returning later to the more complex.

Hydrogen Iodide.—The simplest reaction system for which the most comprehensive data are available is hydrogen iodide. In this system the photodecomposition is unimolecular, indicating that single molecules only are involved in the decomposition process or, in the older mode of expression, the molecules do not act themselves as 'depolarisers' for the activated molecules. The reaction is proportional to the absorbed light energy over a wide variation in the state of the reactant. Thus, Warburg demonstrated this with gaseous pressures varying between 80 and 350 mm.¹² Bodenstein and Lieneweg¹³ extended this observation to liquid hydrogen iodide and quite recently Lewis¹⁴ has reached the same conclusion with gas pressures as low as 0.1 mm. Temperature has no influence on this ratio of absorbed energy to reaction rate. Warburg studied the decomposition with monochromatic radiation of wave lengths $\lambda = 2070, 2530$ and 2820 \AA . These measurements yielded results which are decisive from the standpoint of quantum theory. If we express the results obtained in terms of the number of gram atoms of iodine produced per gram calorie of light energy employed the following values are obtained:

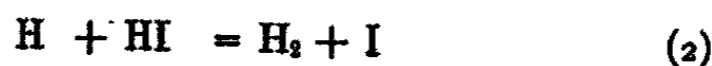
| | | | |
|-----------------------|--------|------|------|
| λ | = 2070 | 2530 | 2820 |
| Mol. I. $\times 10^6$ | = 1.44 | 1.85 | 2.09 |

These results show that, *per gram calorie* of light energy, the extreme ultraviolet is *less* efficient than the longer wave length light. This surprising result, completely inexplicable without quantum theory, becomes, however, immediately understandable, when the quantum relationship is introduced. The calculation then shows that, at each wave length, the number of molecules decomposed per quantum of absorbed energy is 2.0 with a maximum deviation in all of the experiments of not more than 5 per cent, a deviation well within the experimental error. This ratio is also obtained by Bodenstein and Lieneweg for liquid hydrogen iodide at room temperature, for the gas at 150-175°C and by Lewis for the gas at 0.1 mm. pressure. These several results, as well as similar studies with hydrogen bromide, exhibit strikingly, therefore, that the relation between light energy absorbed and chemical reaction produced is a *quantum* relationship.

The quantum absorbed by a hydrogen iodide molecule secures its decomposition. Physical evidence by Tingey and Gerke¹⁵ and by Bonhoeffer and Steiner¹⁶ support this conclusion. But direct experimental evidence by Lewis,¹⁴ showing the independence of the quantum yield of molecular collisions, is decisive that the process of decomposition does not involve a simultaneous reaction of two hydrogen iodide molecules. The measurements already discussed indicate that the photochemical yield corresponds to two molecules of hydrogen iodide decomposed per quantum. It is evident therefore that the primary photo-decomposition must be followed by a series of 'dark' reactions which raise the yield to twice that of the molecules activated by absorption of a quantum. These supervening reactions are *not photo-reactions*. They are purely thermal reactions possible in the given system whether produced initially by photo-action or other means. Their effect is to raise the yield beyond that anticipated upon the basis of absorbed quanta. They offer a fruitful yield for the speculative chemist and have led accordingly to further experimental effort. In the hydrogen iodide case, the simplest of such suggestions which agrees with the experimental facts is that, after the true photochemical reaction,

$$\text{HI} + h\nu = \text{H} + \text{I} \quad (1)$$

the following sequence of reactions occurs:



Bonhoeffer¹⁷ has demonstrated that reaction (2) actually occurs as a purely thermal reaction at ordinary temperatures.

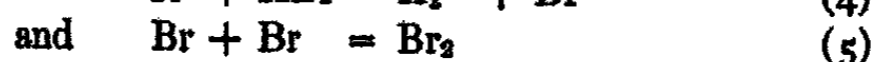
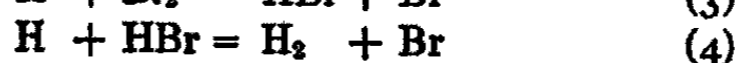
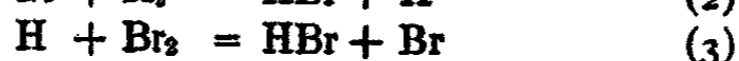
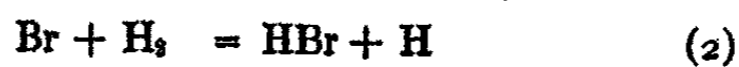
The Hydrogen-Bromine Combination.—When light of a wave length of 5107 Å or less is absorbed by moist bromine, the physical evidence now available shows that the molecule is dissociated into one excited atom and one normal atom. The energy corresponding to a wave length of 5107 Å is approximately 55,700 calories of which 45,200 calories is the energy of dissociation and the residual 10,500 calories is the energy of excitation of the bromine atom.¹ Shorter wave length light corresponding to larger units of energy would produce the same dissociation and the same excited atom, the excess energy being distributed, however, between the two as kinetic energy. It is well known, also, that all attempts to measure directly the concentration of bromine atoms in illuminated bromine vapor have failed to show any marked concentration. It therefore follows that, equating the light energy absorbed to atoms present in the illuminated system would give a ratio in which many millions of absorbed quanta correspond to unit dissociation of bromine. This is not in disagreement with the physical evidence. It only means that the reverse combination of bromine atoms occurs rapidly and that the measurement of atom concentration would only give a stationary state concentration under the given illumination and dependent upon this latter.

If we introduce hydrogen, as an acceptor (or 'depolariser') for bromine atoms produced, we find that the efficiency of the acceptor is dependent on the temperature of the system. It increases with increasing temperature. This means that the thermal processes which succeed the initial photo-process

are dependent upon temperature. Measurements of the quantum yield over such a temperature range will obviously show a remarkable variation. It has been estimated that, at room temperature, more than 100 quanta are absorbed per unit of hydrogen bromide formed. This ratio will also obviously decrease with temperature. At some one temperature it will be unity. Above this temperature it will be greater than unity. This in no way invalidates the physical evidence that one quantum of light energy produces one excited and one normal atom. It only means that the succeeding thermal processes result, with increasing temperature, in increasing production of hydrogen bromide and decreasing recombination to form molecular bromine. In the view of Christiansen, Herzfeld and Polanyi, the following sequence of reactions occurs: firstly, the light reaction is,

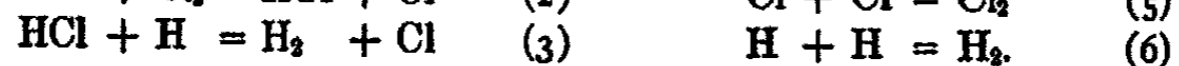
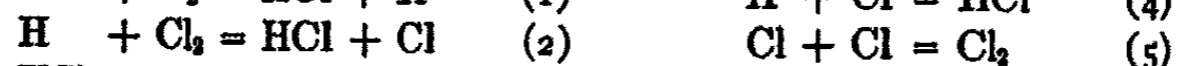


This is then followed by the following purely thermal processes:



Every one of these reactions is known to occur thermally. The investigations of Bodenstein and Lütke Meyer¹⁸ indicated that it is reaction (2) which is temperature-sensitive. The reaction only occurs thermally when the bromine atom and hydrogen molecule together possess an activation energy of about 17,000 calories. Reaction (4) accounts for the inhibiting action of hydrogen bromide. It is not possible here to enter into the extraordinarily interesting correlation by Bodenstein, of his thermal study with Lind⁷ on the formation of hydrogen bromide with that of Bodenstein and Lütke Meyer on the photo-process. It is sufficient if it has been indicated that the evidence from the purely physical side concerning the light-absorption process and its resulting bromine-atom formation supplies a reaction system with which, by purely thermal processes, the known facts of the photo-reaction are completely interpretable.

The Hydrogen-Chlorine Combination.—The same mode of interpretation is applicable to the historical hydrogen-chlorine reaction. The absorption by moist chlorine of light of wave length shorter than $\lambda = 4785 \text{ \AA}$ results in the production of a normal chlorine atom and an excited atom with an energy of excitation corresponding to some 2500 calories. With hydrogen present in the illuminated system, reactions similar to those occurring in the hydrogen-bromine system are possible. Among others we may have:



The essential difference between this and the bromine reaction is that, at room temperatures and upwards, Reaction (1) of the above sequence does not require any activating energy. The thermal reactions are not temperature-

sensitive. This conclusion is in accord with the thermal data, for, in Reaction (1) above, the process involves practically zero heat of reaction whereas the corresponding reaction between bromine atom and hydrogen molecule is endothermic to the extent of 17,000 calories and thus requires activation energy of similar amount. Why the hydrogen chloride does not inhibit the reaction in contradistinction to the action of hydrogen bromide is also explainable by the same set of facts as well as by the direct observation of Bonhoeffer¹⁷ that hydrogen atoms led into hydrogen chloride produce a marked thermal effect, but, the product is only hydrogen and hydrogen chloride without any final production of chlorine.

The extraordinary photochemical yield in the hydrogen-chlorine reaction (ca. 10^6 molecules per quantum) is therefore to be attributed to the facility with which a sequence of thermal reactions can follow the setting up of a reaction system containing atomic chlorine by the quantised process of light absorption.

Photo-sensitised Processes

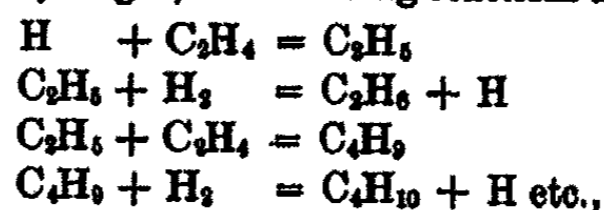
The same attitude may be adopted towards photo-sensitised processes and, in such cases also, there is enough experimental evidence in simple cases to justify the procedure. The photosensitised processes differ from the photochemical processes in that the light-absorbing constituent is not a reactant in the chemical reaction occurring.

Excited Mercury as Sensitiser.—Undoubtedly the simplest of the photo-sensitised reaction processes are those involving excited mercury and hydrogen. For, in these cases, the light quanta involved are monochromatic, of exactly known energy content, producing physical and chemical effects the steps in which have been definitely ascertained. The normal mercury atom absorbs a quantum of mercury resonance radiation corresponding to the wave length 2536 Å and is thereby raised to the 2^3P_1 state, in which it possesses energy equivalent to 112,000 calories of energy. In the absence of foreign gases this energy is re-emitted as fluorescent radiation of the same wave length. With foreign gases present it may lose this energy by collision with the gas molecules without any radiation. If hydrogen be present, the energy transfer results in a photosensitised process, the conversion of molecular into atomic hydrogen with the absorption of 100,000 calories of dissociation energy, the excess 12,000 calories being distributed among the resultants (Hg, 2H) as kinetic energy. The presence of atomic hydrogen may be demonstrated by the 'clean-up' effect,¹⁹ by physical means such as the thermal conductivity of the illuminated system²⁰ or by the chemical reactivity of the atomic hydrogen.²¹

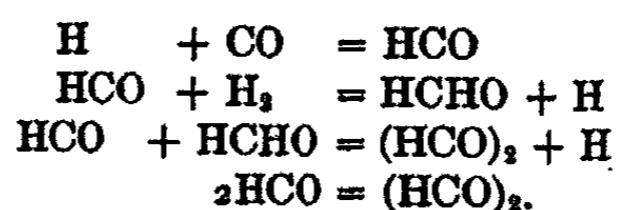
Were the experiment possible, the ratio between the number of quanta absorbed by the mercury atoms and the number of hydrogen atoms produced by subsequent collision might be ascertained. This would be the photochemical yield of the process. We know it would depend on the hydrogen pressure, since the extinction of the fluorescence is dependent on this pressure and increases with increasing pressure. With sufficiently high hydrogen

pressures we can conclude that every excited mercury atom should lead to the production of two hydrogen atoms. Any attempt to ascertain the ratio of quanta absorbed to atoms produced either by the 'clean-up' effect or by means of thermal conductivity would certainly yield a result less than two atoms per quantum since either method would fail to correct for the thermal recombination of hydrogen atoms formed.

Attempts by chemical means to ascertain the number of atoms formed per quantum absorbed would be subject to the same limitations that the hydrogen-halogen photo-reactions, already discussed, suffer. The thermal processes possible would determine the yield obtained. This has already been demonstrated experimentally in a number of cases. Thus, if ethylene is introduced as the acceptor for atomic hydrogen, the following reactions are possible



and the yield in terms of saturated hydrocarbons formed will be determined by the length of such sequences. The same is true with oxygen as acceptor where hydrogen peroxide is produced and with carbon monoxide where formaldehyde and glyoxal²² are identified products, probably by such sequences as



In all these cases the yield is not determined by the light quanta absorbed but by the reactivity of the system produced by the absorption process.

The Photo-sensitised Decomposition of Ozone.—The decomposition of ozone may be photosensitised to visible light by introducing chlorine or bromine into the gas. In either case the initial light absorption process by the halogen molecule must yield one excited and one normal atom. But, the subsequent yield of decomposed ozone is quite different in the two cases. As Bonhoeffer²³ has shown, only two molecules of ozone are decomposed per pair of chlorine atoms produced, whereas as many as thirty ozone molecules decompose per pair of bromine atoms resulting from light absorption. The explanation of this difference must lie in the different reactivities of the chlorine atom-ozone system and the bromine atom-ozone system. No one has yet indicated what these differences are or attempted other methods than photo-chemical of studying them. It is possible that some progress might be made in this regard by a study of the effect of temperature on the photo-sensitised processes.

The Stationary State

Several examples have already been discussed in which the absorption of light by a reactant results in the displacement of the system from its normal 'dark' equilibrium. The physical evidence indicates that in both illuminated

chlorine and bromine there exists a greater concentration of atoms than is present in the unilluminated system at the same temperature. The penetrating analysis of the hydrogen-bromine combination by Bodenstein and Lütkemeyer¹⁸ permitted a calculation of the respective 'dark' and 'illuminated' bromine atom concentrations at 218°C. The results showed that, for the intensity employed, approximately 300 times the concentration of atoms was present in the illuminated system. The stationary concentration was determined in part by the recombination of atoms to form molecules and, on the assumption that each quantum absorbed yielded two atoms, only about 0.0013 of all atomic collisions led to the formation of molecules. Had the quantum efficiency been calculated from the stationary state concentration the efficiency of the absorbed quanta would have been negligibly small.

There are a number of other reactions in which it is experimentally possible to determine the rate of the photo-reaction resulting in the displacement of equilibrium, independently of the dark reactions occurring simultaneously. These include the decomposition of nitrosyl chloride, the equilibrium, $Fe^{2+} - Fe^{3+}$, $I_2 - I'$, the polymerization of anthracene and substituted anthracenes. It is not possible to detail these in the scope of this article. One must suffice as an example.

The Equilibrium $Fe^{2+} - Fe^{3+}$, $I_2 - I'$.—Rideal and Williams²⁴ discovered that the rate of reaction in the initial stages of illumination of the thermal equilibrium solution, when the dark reactions compensate each other, provided a means of dissociating the photo-process from the thermal processes. In this way they were able to show that one molecule of iodine reacted per absorbed light quantum (5790 Å). Kistiakowsky²⁵ showed that this was true also of the light of wave lengths 5460 Å, 4360 Å and 3660 Å. In each case the relation was one molecule of iodine reacting per absorbed quantum. This situation is entirely analogous to that discussed in the case of hydrogen iodide. Without quantum theory, one has to explain why 78,500 calories of light energy of wave length 3660 Å is only as efficient as 43,850 calories of the longer wave length 5790 Å. Immediately the quantum concept is introduced this difficulty entirely disappears. There is an exact relation between the quantum absorbed and the activated molecules, and the method of study in this case eliminates the complicating thermal reactions which would mask the relation.

Inhibition

The necessity of distinguishing between the absorption act with its immediate chemical consequence and the chemical, purely thermal, reactions which succeed it, is nowhere more evident than in photo-reactions which show the phenomenon of inhibition. The classical example of inhibition in a photo-reaction process is the influence of oxygen on the yield of hydrogen chloride in the hydrogen-chlorine combination. We have recorded above that a large number of thermal reactions may succeed the original absorption act in this case and produce yields of the order of $10^5 - 10^6$ molecules of hydrogen chloride per quantum of absorbed light. Oxygen reduces the yield to an extent roughly proportional to its concentration so that hydrogen-chlorine mixtures

containing one per cent of oxygen are only feebly sensitive to illuminations which would produce explosions in the oxygen-free gas. The role of the oxygen in the process is still under discussion and no completely satisfactory conclusion has yet been reached. From the small concentration of oxygen required it is evident that the effect of the oxygen is exerted either on the atomic chlorine produced by the absorption act or on the thermal reactions subsequently produced.

The phenomenon of inhibition is not, however, confined to those photo-reactions for the explanation of which the reactivity of atomic species may be invoked. Thus, the photo-decomposition of aqueous hydrogen peroxide²⁶ and numerous examples of auto-oxidation such as those of benzaldehyde and of aqueous sodium sulphite solutions all show the phenomenon. It has now been shown by Bäckström²⁷ for all the auto-oxidations thus far investigated that the yield of oxidation product is many thousand-fold that to be anticipated on the basis of equivalence between molecules oxidised and quanta absorbed, thus confirming a prediction of Christiansen.²⁸ In the case of benzaldehyde the yield is approximately 10,000 molecules per quantum. With sodium sulphite the ratio rises to 50,000 molecules per quantum, an extremely striking result when it is remembered that this occurs in aqueous solution where there are more than 55 molecules of water for every molecule of sulphite (i.e., less than 1 Molar Sulphite solution). It is evident that there must follow the initial absorption act a whole series of thermal reactions producing sulphite oxidation. This agrees with the fact that even the purely thermal oxidation of benzaldehyde and sodium sulphite are also sensitive to inhibitors. The mechanism of the action of the inhibitor is only in the initial stages of study but unpublished results now available in Princeton indicate an intimate relationship between the amount of sulphite oxidised and the amount of inhibitor oxidised. The sulphite oxidised is inversely proportional to the concentration of inhibitor. The inhibitor oxidised is, however, *constant* over a very wide concentration range and with various alcohols as inhibitors, even though the inhibitor efficiency varies markedly. There is evidence that the amount of inhibitor oxidised is of the order of 1/5000 of the sulphite which would have been oxidised had the inhibitor not been present. This evidence points overwhelmingly to the conclusion that, in the reaction without inhibitor, the initial photo-process is succeeded by a large number of thermal reactions which can be stopped by causing the energy-rich reaction products of the auto-oxidation process to oxidise the inhibitor. The stages of the auto-oxidation process have been studied in detail by Backstrom. On this basis, the phenomenon of inhibition becomes a special case of the well-known phenomenon of induced oxidation.

In the case of hydrogen peroxide solutions, the mechanism of the thermal processes have not been elucidated in detail. The extent of decomposition yield in the photo-process and the inhibitions of the purely thermal decomposition point, however, to the existence of thermal chain reactions.

Complex Photo-processes

We have seen that even in the relatively simple reaction systems already discussed there are still problems which have not yet received their final solution. It has been shown, however, that the method of approach here developed, of distinguishing between, on the one hand, the initial absorption act and its immediate chemical consequences and, on the other hand, the thermal reactions possible in a system thus photochemically produced, leads to an understandable interpretation of the total process. With more complex systems the difficulties increase since the factors to be controlled increase. Nevertheless, it can be shown, with one or two examples from these more complex processes, that the same guiding principles hold.

Oxidation of Quinine.—The classical researches of Luther and Forbes²⁹ on the photo-oxidation of quinine in presence of chromic acid are of use in this regard. In absence of chromic acid the light absorbed by quinine is re-emitted as fluorescence radiation. No photochemical reaction occurs. With small amounts of chromic acid present, a portion of the energy absorbed by the quinine is consumed in producing fluorescence and the residue in promoting reaction between active quinine molecules and chromic acid. In such cases it follows that the absorbed quanta are considerably in excess of the reacting molecules. With increase in chromic acid concentration, the probability of a quinine molecule losing an absorbed quantum as fluorescent radiation decreases and, hence, at a given acid concentration and beyond, a state of affairs obtains in which reaction with chromic acid follows immediately upon the absorption act. In such case there will be an equivalence between quinine molecules oxidised and quanta absorbed by quinine. There is, however, a complicating factor in that such a relation does not exist between reaction and total light absorbed since chromic acid absorbs but is not thereby converted into a reactive species. One further consequence of this also follows. In large excess of chromic acid, where the light is practically screened from the quinine, the photochemical yield would fall again from unity to practically zero.

Reduction of Fehling's Solution.—Another factor which influences the yield in processes initiated by light may be illustrated by the case of Fehling's solution. Byk³⁰ showed that the photo-decomposition of the solution itself was secured by light of frequencies in the ultraviolet absorbed by the cupri-complex present. No decomposition occurs if the solution is illuminated by the blue light of the visible absorption band. The system under these conditions is entirely analogous to the quinine system in absence of chromic acid. The absorbed radiations are transformed into radiation of other wave lengths (or otherwise dissipated). If, however, as Leighton³¹ showed, hydroquinone be introduced into such solutions illuminated by red light, reaction occurs and reduction takes place. The hydroquinone plays the part of the chromic acid in the quinine reaction. With increase in its concentration the photo-yield may be expected to rise from zero to unity as in the quinine case also.

Other complex systems will doubtless yield to patient and intelligent investigation; without this latter no progress can be expected.

Einstein's Law of Photochemical Equivalence

We are now in a position to examine the law of photochemical equivalence enunciated by Einstein in 1912 in the light of the yield of fifteen years of experimental study. The examples discussed in the preceding, together with many others which might have been cited, all suggest that the coupling of the concept of quantised absorption with the idea of net photochemical yield has not been sustained by the experimental test. The idea of photochemical equivalence which the title of the law suggests has not been confirmed by this practical work. Indeed, in the case of some workers, this suggestion of equivalence has given rise to mistrust of the general idea of quantised absorption which is basic to all these modern studies of photochemical processes and is demanded by physical theory.

It would therefore seem desirable to attempt a generalisation of the facts concerning the mechanism of the photochemical process which, while avoiding the difficulties inherent in the acceptance of the Law of Photochemical Equivalence as originally formulated would embody the elements of this law which have found support from its study. For this purpose it seems necessary first to avoid entirely the name which has become usual in reference to this matter, since equivalence has been demonstrated only in exceptional cases rather than as a general rule.

The situation may be met by means of two laws of photochemistry. The First Law of Photochemistry would be the Grothuss-Draper Absorption Law, embodied in the statement that: Only light that is absorbed is effective in producing chemical change. This would be followed by the *Second Law of Photochemistry* which might thus be expressed:

The absorption of light is a quantum process involving one quantum per absorbing molecule (or atom). The photochemical yield is determined by the thermal reactions of the system produced by the light absorption.

Of this second law, the quantum concept of absorption is Einstein's contribution to the progress of photochemistry. The second half is a generalisation from the experiments of numerous workers who, in testing Einstein's original ideas, have added enormously to the quantitative knowledge of mechanism in photochemical processes and demonstrated the factors which determine the yield from a given illuminated system.

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²⁰ Sentfleben: *Z. Physik*, 32, 922 (1925).
²¹ Cario and Franck and others: See Taylor: *J. Am. Chem. Soc.*, 48, 2840 (1926).
²² That glyoxal is also produced was kindly communicated to me verbally by Dr. W. Frankfurter of the I. G. Laboratories at Oppau, Germany.
²³ Bonhoeffer: *Z. Physik*, 13, 94 (1923).
²⁴ Rideal and Williams: *J. Chem. Soc.*, 127, 258 (1926).
²⁵ Kistiakowsky: *J. Am. Chem. Soc.*, 49, 976 (1927).
²⁶ Anderson and Taylor: *J. Am. Chem. Soc.*, 45, 650 (1923).
²⁷ Bäckström: *J. Am. Chem. Soc.*, 49, 1460 (1927); *Medd. K. Vet. Akad. Nobel Inst.*, 6, Nos. 15 and 16 (1927).
²⁸ Christiansen: *J. Phys. Chem.*, 28, 145 (1924).
²⁹ Luther and Forbes: *J. Am. Chem. Soc.*, 31, 770 (1909).
³⁰ Byk: *Z. physik. Chem.*, 49, 659 (1904).
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THE DISPLACEMENT OF EQUILIBRIUM BY LIGHT

BY WILDER D. BANCROFT

Before we can discuss profitably the displacement of equilibrium by light, it is necessary to be clear as to the general principles underlying the chemical action of light. In 1818 Grotthuss formulated the law that only that light which is absorbed by a substance can cause chemical change. This law was subsequently rediscovered by Draper and is often referred to as Draper's law. So far as we know, there are no exceptions to this law. A striking illustration of it is the behavior of a green alcoholic solution of chlorophyll in presence of air when exposed to magnesium light for half an hour behind a screen of potassium bichromate or one of ammoniacal copper sulphate. The color bleaches in the first case and not in the second. Herschel has studied cases where infra-red light causes chemical change.

While all light which is absorbed tends to produce a chemical change, all rays are not equally effective. It is well known that the ordinary photographic plate is much more sensitive to blue and violet light than it is to red and yellow. For this reason we get practically no action when photographic paper is exposed to magnesium light behind a solution of potassium bichromate and marked blackening when the light is transmitted through a solution of ammoniacal copper sulphate. Patent blue and Fehling's solution can be decomposed by light corresponding to the absorption in the ultra-violet but are apparently insensitive under ordinary conditions to light corresponding to the band in the red and yellow. It is rather the fashion nowadays, to account for the alleged greater efficiency of the ultra-violet light by saying that the quantum, $h\nu$, is larger the higher the frequency or the shorter the wave-length, and that consequently the greater energy is more effective.¹ The difficulty with an explanation of this sort is that it is a general one and therefore must be true in all cases. There is some evidence that it is not true for chlorophyll and consequently it is safer, for the present, merely to say that the chemical efficiency of different rays absorbed by a given substance is not necessarily the same and that, in many cases, light of short wave-length is more effective than light of longer wave-length.

We get all degrees of sensitiveness to light. Under ordinary conditions copper sulphate solutions are absolutely stable in light. Certain other solutions are stable so far as permanent changes are concerned; but undergo some change because they fluoresce under the influence of light. Many solids phosphoresce when exposed to light, and the existence of the time factor is in itself evidence of some change in the substance, even though we may not be able at present to say definitely what that change is. Water is absolutely

¹ H. S. Taylor (preceding paper) says that with iodine the extreme ultra-violet is less effective per gram calorie of light absorbed than the longer wave-lengths because the gram-calorie is a smaller fraction of the quantum, the higher the frequency. He does not explain why Fehling's solution is less sensitive in the red and yellow than in the violet.

stable so far as the visible spectrum is concerned; but it can be decomposed to some extent by ultra-violet light. Alcohol is decomposed very slowly by ultra-violet light at ordinary temperatures and quite rapidly at higher temperatures.

A potassium bichromate solution is stable to light of the visible spectrum when pure; but decomposes in presence of suitable organic material. We get some blackening of silver salts even when practically pure and more when organic matter is present. Many dyes are bleached by light in presence of air. Light decomposes mercurous chloride even in the absence of air, and Eder's solution of mercuric chloride dissolved in ammonium oxalate solution is used for the measuring of light. A mixture of hydrogen and chlorine reacts under the influence of light which is absorbed by chlorine. Carbon monoxide and chlorine react to form phosgene, COCl_2 . Hydriodic acid gas is decomposed by light, blue light being especially effective. This should mean that hydriodic acid has an absorption band in the blue; but I have never seen any statement to that effect. The matter should be investigated because there is always a possibility of a sensitization directly or indirectly by iodine.

In the original paper by Grotthuss in 1818 he stated that the action of light is analogous to that of a voltaic cell. This has recently been put forward by Baur¹ without any reference to Grotthuss. "Photolysis is a molecular electrolysis." I discussed this view at some length fifteen years ago.²

"While the statement that light acts as a voltaic cell has proved to be an excellent working hypothesis for cases involving oxidation and reduction, its usefulness is not so striking in cases involving allotropic modifications or polymerization. It is true that Berthelot³ has shown that soluble sulphur can be obtained at the anode by electrolyzing a solution of hydrogen sulphide and that insoluble sulphur can be obtained at the cathode by electrolyzing a solution of sulphuric or sulphurous acid; but the light is acting on sulphur and not on hydrogen sulphide or sulphurous acid. This did not bother me seriously at one time; but I then expected to prepare dianthracene electrolytically.⁴ This has been tried and we have not been successful. As that was admittedly a crucial test, I am prepared to abide by the result. It is also not absolutely satisfactory to have to say, in the case of organic substances, that light produces the same decomposition products that we should get if we could electrolyze the substance in question. It is quite possible that these difficulties may be overcome and that somebody may prepare dianthracene electrolytically.

"There is another more serious objection to the Grotthuss generalization in its present form. The selective action of light is much more marked than the selective action of the current. We can take a solution containing cadmium and copper sulphates and we can precipitate metallic copper by regulating the voltage. We cannot, however, precipitate cadmium from that

¹ Trans. Faraday Soc., 20, 627 (1925).

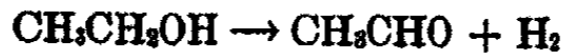
² Bancroft: Eighth Int. Congress Applied Chemistry, 20, 31 (1912).

³ Ann. Chim. Phys., (3) 49, 448 (1857).

⁴ Trans. Am. Electrochem. Soc., 13, 257 (1908).

solution before the copper, though we can do it if we change to a cyanide solution. Suppose that we have two dyes of different colors which are oxidized about equally readily. By changing the wave-length of the light we can cause one dye or the other to oxidize in the air. So far as I know the only analogy to this in electrochemistry is the reduction of nitrates and nitrites.¹ At a smooth platinum cathode nitrite is reduced more readily than nitrate while the reverse is true at a spongy copper cathode. One difference between light and the electric current is that the current is a single reagent except in so far as the specific nature of the electrode may make a difference, while light is a mixture of reagents. Light of one wave-length may act on one substance and light of another wave-length on another, or lights of different wave-lengths may cause the same substance to react in different ways. This is not covered by the Grotthuss formulation and it is therefore necessary to make a more general statement."

The only thing that I should care to add to this quotation is that light of different wave-lengths can apparently decompose alcohol in at least two different ways:



While it would probably be a relatively simple thing to arrange a cell which would cause hydrogen and acetaldehyde to react with the formation of alcohol, I do not at present see how one could do anything similar with water and ethylene.

In 1905 I gave a formulation for electrolysis² which I have since found helpful. "In the case of electrolysis the only specific action which we have to attribute to the current is that it tends to set free the anions at the anode and the cations at the cathode. What happens over and above that is a question of chemistry depending on the reaction velocity and equilibrium relations in each particular case."

Three years³ later I wrote with reference to light: "The chemical effect of the light is merely to eliminate, if possible, the substance absorbing the light. Whether that elimination takes place as a result of oxidation or of reduction is a matter which is quite independent of the light and which depends on the nature of the depolarizer. If the depolarizer is a sufficiently strong reducing agent, we get reduction by light. If the depolarizing agent is a sufficiently strong oxidizing agent, we get oxidation by light. If it is not sufficiently one or the other we get no action by light. A very good instance of the variable action of light is to be found in the case of mercurous chloride. In the presence of a sufficiently powerful reducing agent, light reduces mercurous chloride to metallic mercury. In the presence of a sufficiently powerful oxidizing agent, light oxidizes mercurous chloride to mercuric chloride. If there is no

¹ Müller and Spitzer: *Z. Electrochemie*, **11**, 509 (1905).

² Bancroft: *Trans. Am. Electrochem. Soc.*, **8**, 33 (1905).

³ Bancroft: *Trans. Am. Electrochem. Soc.*, **13**, 246 (1908).

more suitable depolarizer, the mercurous chloride itself acts as a depolarizer and is changed to mercury and mercuric chloride."

In 1912 I proposed the following generalization¹ as an improvement on the two laws of Grotthuss: "All radiations which are absorbed by a substance tend to eliminate that substance. It is entirely a question of chemistry whether any reaction takes place or what the reaction products are."

Since people do not, even now, think and talk in terms of depolarizers, it will be wise to discuss them more in detail. We distinguish between chemical depolarizers or sensitizers and optical ones. The action of the chemical depolarizer is quite simple. If we take a ferric chloride solution and expose it to light, we might hope to get ferrous chloride and chlorine; but the two could not coexist and therefore would be formed only to a slight extent, if at all. If we take an alcoholic solution of ferric chloride, the chlorine can react with the alcohol. It therefore takes less energy to reduce or decompose ferric chloride in alcoholic solution. Actually, we do get a photochemical change under these conditions. Alcohol or gelatine will act as a depolarizer for bichromate solutions. Chlorophyll and many dyes can react with the oxygen of the air under the influence of light. If we took a more powerful oxidizing agent, we could get a bleaching in the dark. With a weaker oxidizing agent we should have to use a more intense light and might not get oxidation even then. In presence of oxalic acid as depolarizer² we can get tellurium, selenium, and sulphur photochemically from solutions of telluric, selenic, and sulphurous acids respectively. In presence of air ferrous sulphocyanate solutions are oxidized to ferric sulphocyanate under the influence of light.

We can reduce many dyes photochemically in presence of a suitable amount of sodium or calcium hydrosulphite and we can oxidize them photochemically in presence of hydrogen peroxide. It is quite obvious that, in general, addition of a reducing agent will increase the tendency of a dye to reduce under the action of light, while addition of an oxidizing agent will increase the tendency to photochemical oxidation.

In some cases there is the unexpected result that addition of certain reducing agents increases the sensitivity of certain dyes to photochemical oxidation in presence of air. Thus methylene blue is readily oxidized photochemically by air when in presence of anethol or sodium bisulphite, both of them reducing agents. Nobody has worked out the theory of this; but it seems probable that part of the oxygen goes to the anethol and part to the methylene blue.

Byk³ has shown that ultra-violet light of wave-lengths somewhere between 350 $\mu\mu$ and 400 $\mu\mu$ cause the precipitation of cuprous oxide from a specially prepared Fehling's solution, while no rays of the visible spectrum cause any decomposition. "If that is the case, the precipitation of cuprous oxide must be prevented by the use of a ray filter which cuts off the ultraviolet. As a

¹ Bancroft: Eighth Int. Congress Applied Chemistry, 20, 33 (1912).

² Benrath: Chem. Ztg., 39, 25 (1915).

³ Z. physik. Chem., 49, 659, 679 (1904).

matter of fact, a one percent solution of quinine sulphate acidified with a little sulphuric acid protects Fehling's solution from the action of the sun's rays. The active rays are therefore really in the ultra-violet. In addition to an upper limit of about $400\ \mu\mu$ for the wave-length of the active light, we can also give a lower limit. According to Precht¹ a tartrazin solution absorbs chiefly the wave-lengths $495\ \mu\mu$ - $362.5\ \mu\mu$, but cuts down the rays as far as $352.5\ \mu\mu$. Since tartrazin protects Fehling's solution, the active wave-lengths must be above $350\ \mu\mu$ and there must be a maximum sensitiveness between $400\ \mu\mu$ and about $450\ \mu\mu$.

By adding a suitable amount of hydroquinone to Byk's Fehling solution, Leighton² obtained a solution which did not decompose in the dark but which was reduced by red light. Bennett³ has shown that it is possible to add to a copper sulphate solution a solution of white phosphorus of such strength that there was no reduction in any reasonable time in the dark whereas there was a reduction in the light to copper which then reacted with the excess of phosphorus to form copper phosphide. Since a copper sulphate solution is a typical case of a deeply colored one which is ordinarily absolutely stable to light, this experiment is satisfactory proof that light of any wave-length which is absorbed tends to eliminate that substance.

Henri and Wurmser⁴ have studied a case which may differ in principle from that of hydroquinone. They find that acetaldehyde shows strong absorption and strong chemical action for light of wave-length $277.5\ \mu\mu$, and strong absorption and weak chemical action for light of wave-length $220\ \mu\mu$. They account for this by assuming that the first absorption is due to the aldehyde group and the second to the methyl group. This matter should be studied more carefully.

It is well known that some lithopones (zinc sulphide and barium sulphate) blacken in the light and it was shown by O'Brien⁵ that this was due to the formation of metallic zinc adsorbed by barium sulphate. This work has been repeated on a larger scale by Job and Emschwiller,⁶ who used a phosphorescing zinc sulphide and isolated more zinc than O'Brien did.

The production of the latent image on the photographic plate used to worry people a good deal. From energy considerations Hurter and Driffield believed⁷ that it was impossible for a weak light to set free any silver from silver bromide. "That any ordinary camera exposure is inadequate to produce a material decomposition of the silver bromide on the plate can be shown by other experiments and considerations. A standard candle consumes 120 grains or 7.77 grams of spermaceti per hour, or about 0.0021 grams per second. The energy evolved by the combustion of 0.0021 gram spermaceti

¹ Z. wiss. Phot., 1, 262 (1903).

² J. Phys. Chem., 17, 205 (1913).

³ J. Phys. Chem., 16, 782 (1912).

⁴ Compt. rend., 156, 230 (1913).

⁵ J. Phys. Chem., 19, 113 (1915).

⁶ Compt. rend., 177, 313 (1923).

⁷ Phot. J., 22, 149 (1898).

(1 gram = 10000 units of heat) is 21 gram-units (small calories). If the whole of this energy were produced in the form of chemically active light and evenly distributed over a sphere of one meter radius = 12,663 sq. cm., the amount

of energy per sq. cm. of surface would be $\frac{21 \times 100}{125,663} = 0.016$ gram-units of heat.

"While it is possible on a sensitive plate to produce a deposit of 26.5 milligrams of metallic silver per 100 sq. cm. area by an exposure of 10 C.M.S., the amount of energy received by this area, assuming the whole energy yielded by the candle to be taken into consideration, as in the above calculation is $10 \times 0.016 = 0.16$ units in ten seconds. Now the decomposition of silver bromide equivalent to 108 milligrams of silver is 5.6 units, so that the candle, even if the whole of its energy of combustion were active in decomposing silver bromide, could only decompose 2.9 percent of the amount which experiment shows can be actually rendered amenable to development. As a matter of fact, however, only a small fraction of the energy of the candle is transformed into radiant energy; and again, a very small fraction of the radiant energy constitutes ethereal waves of sufficiently short wave-length to affect silver bromide. It is thus rendered quite evident that the candle can only furnish an infinitesimal part of the energy necessary to produce 26.5 milligrams of metallic silver per 100 sq. cm. with an exposure of 10 C.M.S., and that the whole of this energy is, in all probability, provided by the developer.'

Hurter and Driffeld evidently believed in the all or none principle. Since the developer admittedly did something, it must do everything. These difficulties are very real if we assume reduction to silver sub-bromide and still more serious if the silver bromide is reduced to free metallic silver. They vanish entirely on the basis of the adsorption theory, because the difference in the energy content of the undecomposed and the decomposed silver bromide can theoretically be made as small as one pleases. Practically, the difference which can be detected depends upon the sensitiveness of the developer.

When opening the general discussion by the Faraday Society on "Photochemical Reactions in Liquids and Gases," Professor Allmand¹ said: "The application of the quantum theory to photochemistry dates in practice from the enunciation by Einstein in 1912 of the so-called 'photochemical equivalent law,' a law, which, stated in its baldest terms, says that, in a photochemical reaction, one quantum of active light is absorbed per molecule of absorbing and reacting substance which disappears. This simple and attractive relation, put forward with the authority of Einstein, has proved a great stimulus to research in a somewhat neglected field of chemistry, and a field, moreover, in which an *impasse* seemed to have been reached in respect of such matters as the primary mechanism of photochemical change, the significance of the part played by the absorbed light, and the whole question of the classification of photochemical reactions. In this sense then, the relation has proved itself a working hypothesis of great value."

¹ Trans. Faraday Soc., 20, 438 (1925).

Fortunately for my peace of mind it does not come within the scope of this report to discuss the general accuracy of the Einstein equation; but it has been rather a surprise and a grief to me to find so many people working hard over possible chain mechanisms before they are absolutely certain of the accuracy of their premises. Suppose we take a reaction which does not go in the light in the absence of a depolarizer and which goes in the dark in the presence of a sufficient concentration of the depolarizer. If we expose the system for a given length of time to a given intensity of light and vary the concentration of the depolarizer, what quantitative relations shall we find, for the case that the absorption of the effective light by the depolarizer is negligible? Shall we get one quantum per molecule as soon as a reaction occurs and will it stay constant until the reaction takes place or shall we get an increasing efficiency of light with increasing concentration of the depolarizer? I have never seen any account of such an experiment or any reference to such an experiment and yet such measurements should be made with a large number of reactions because they are absolutely fundamental and because the results are independent of any assumption as to the mechanism of the photochemical reaction.¹

We can now consider optical sensitizers,² which might be called depolarizers with marked absorption bands. In 1873 H. W. Vogel was studying the effect of the solar spectrum on silver chloride, bromide, and iodide films. In one of his experiments he used an English silver bromide dry plate which had been stained yellow with aniline red to prevent halation. This plate showed a second maximum of sensitiveness in the green. Further investigation showed that this second maximum of sensitiveness corresponded to an absorption band in the spectrum of a solution of aniline red and that the abnormal behavior of the plate disappeared if the dyestuff were extracted with alcohol. This showed a relation between the sensitiveness of a silver bromide plate for certain wave-lengths and the absorption band for one dye. Vogel proceeded to test the matter further.³

"I made experiments, now, to see whether other dyes behaved similarly and whether they made silver bromide sensitive for those rays which they absorbed. I first tried coralline. A dilute solution of the same shows in the spectroscopie an absorption band, like that of aniline red, between D and E; *it absorbs the yellow and the yellowish-green light*. On the other hand blue passes to a considerable extent. If the sunlight passes through the coralline solution and then through a prism; green and yellow are missing from the resulting spectrum. There is a dark absorption band in the place where yellow and green are usually to be seen.

"I now dissolved coralline in alcohol and added it to my collodion emulsion so that the latter was dyed a deep red. From this collodion, silver bromide

¹ Since this was written H. S. Taylor (preceding paper) says that the number of molecules decomposed per quantum will vary from zero to unity with increasing concentration of the depolarizer. Barring some new factor, the upper limit should be infinity and not unity.

² For additional details, see Bancroft: *J. Phys. Chem.*, 12, 318 (1908).

³ H. W. Vogel: "Handbuch der Photographie," 4th Ed. 1, 204 (1890).

dry plates were prepared which were dyed distinctly red. When these were exposed to the spectrum, my prediction was fulfilled. *The plates were sensitive in the indigo, the sensitiveness decreasing in the direction of the clear blue and becoming very slight at F. From there on the sensitiveness increased, becoming nearly as marked in the yellow as it was in the indigo.* A means had thus been found of making silver bromide plates which should be acted on just as readily by the yellow, which had hitherto been considered a chemically inactive color, as by the indigo, which had previously been considered the spectrum color producing the greatest chemical effect.

"From these experiments I was justified in concluding that some other substance would increase the sensitiveness of silver bromide for the red provided that substance absorbed the red to a marked extent. Such a substance I found among the green aniline dyes. It absorbed the red rays pretty thoroughly between the lines D and C; at higher concentrations, the absorption extended beyond D. Yellow, green and blue passed through with practically no absorption. A collodion dyed with this green proved in fact to be sensitive to light down into the red.

"The sensitiveness decreased gradually from the indigo to the yellow and was almost nothing in the orange. From this point the sensitiveness increased becoming very marked in the red just where the absorption band occurred.

"From these experiments I feel justified in concluding with a good deal of certainty that we are able to *make silver bromide sensitive to any desired color, or to increase its existing sensitiveness for certain colors. It is only necessary to add a substance which will promote the decomposition of silver bromide and which absorbs the rays in question, letting the others pass. The aggravating difficulty in regard to the photographic ineffectiveness of certain colors appears to be a thing of the past.* . . .

"This conclusion met with little favor at first. Distinguished investigators, like Schultz-Sellaack,¹ Monckhoven, Carey Lea² and Abney, tried to show that the author's results were wrong. In the *British Journal of Photography* for 1874, the discovery of the author was jeered at and made fun of.³ The Berlin Academy of Sciences, however, recognized the importance of these results and made a considerable grant to the author to enable him to carry on his investigations and to procure suitable spectrum apparatus.

"The reason for the protracted opposition to the author's results is partly due to the fact that very few people at that time were clear as to the connection between chemical action and absorption. Even in 1876 Abney assumed that those rays acted the most on a photographic plate which were transmitted the most completely. Also, there was a widespread ignorance in regard to absorption spectra. Then, too, the majority of those, who tried to duplicate the author's results, failed because they dyed the films too heavily

¹ Ber., 7, 386 (1874). As the text shows, there is absolutely no truth in the assumption recently advanced that it was Schultz-Sellaack's investigations which caused the author to study the effect of dyes on collodion.

² Although Lea fought the author's results obstinately, he is now, curiously enough, spoken of as one who helped to develop color-sensitive photography.

³ Photogr. Mittheilungen, II, 100.

and exposed them for much too short a time. Finally the dyes available at that time were so impure that the silver baths or the collodion emulsion, as it was then prepared, soon became spoiled. As far as the introduction of the principle into commercial practice was concerned, the prospect seemed at first absolutely hopeless. The author himself only obtained one good plate to five bad ones."

There is no question nowadays about the existence of optical sensitization. Sensitizing dyes are used in all forms of panchromatic or orthochromatic plates and in many plates used for special purposes. In order to minimize the difficulties due to haze in aerial photography the Eastman Kodak Laboratory has perfected a dye which sensitizes so well that it is possible to take aerial photographs through a red screen with exposures as short as one one-hundredth of a second. The theory of the process has not kept pace with the empirical progress of the art.

There is no explanation at all for the behavior of the different silver halides, though Vogel obtained some facts. Silver chloride collodion dyed with naphthalene red "showed a sensitiveness which corresponded almost exactly to that of the human eye for blue and red. Further experiments established the surprising fact that many dyes, which worked admirably with silver bromide collodion, did not produce the same effect on silver chloride collodion. This is true for magenta, for instance. It makes silver bromide very sensitive to yellow, and affects silver chloride much less. Naphthalene red acts equally well with both salts. These dyes act also upon silver iodide but to a very much lesser extent."

Bothamley¹ has given a pretty fair summary of our knowledge in 1895. "Although large numbers of dyes have been examined since Dr. H. W. Vogel's discovery in 1873, very few exert any marked effect in making gelatino-bromide plates sensitive to the less refrangible rays of the spectrum. Only cyanin and the dyes of the eosin group (including the rhodamines), with perhaps malachite green, chrysoidine, and alizarin blue, can be said to exert any useful effect.

"The main points established by previous observers may be summarized as follows: (1) The dyes that act as sensitizers are readily affected by light when they are in contact with fabric, paper, etc.; (2) in order that a dye may act as a sensitizer it must have the power of entering into intimate union with silver bromide, forming a kind of 'lake'; (3) and it must show a strong absorption band for the particular rays for which it is to sensitize. Although these statements hold good for all the dyes that are known to act as sensitizers, it is important to observe that the converse is not necessarily true. Several dyes having all these properties show no appreciable sensitizing action.

"Experiments by Dr. E. Vogel on the rate of fading and the sensitizing action of the eosin dyes, led him to the conclusion that the order of sensitizing effect coincides with the order of fading when the dyes are exposed to light.

¹ British Association Reports, 1895, 661.

The order in which Vogel places the dyes does not, however, correspond with the order of fading as observed in dyed fabrics, and the experimental method that he used is open to criticism.

"The author's observations on the fading of the various sensitizers, when exposed to light in contact with gelatin, led him to the conclusion, that although all the sensitizers are readily affected by light, the order of sensitizing effect does not necessarily correspond with the order of fading, whether the dyes belong to the same chemical group or not.

"There are two chief hypotheses as to the mode in which the dyes act, namely: (1) the view held by Abney that the dye itself is oxidized by the action of light, the oxidation product remaining in contact with the silver bromide; and when the plate is treated with the developer, the latter and the oxidation product acting simultaneously on the silver bromide bring about its reduction; and (2) the view first definitely formulated by Eder, and endorsed by Vogel, namely, that the energy absorbed by the dyed silver bromide is partially used up in bringing about the chemical decomposition of the silver bromide, instead of being almost entirely converted into heat, as when absorbed by the dye alone.

"The author has found that the less refrangible rays will produce a photographic image on the sensitized gelatino-bromide plates, when they are immersed in powerfully reducing solutions, such as a mixture of sodium sulphite and pyrogallol. This holds good for cyanin, the eosin dyes, the rhodamines, and quinoline red, whether the sensitizer has been added to the emulsion or has been applied to the prepared plate in the form of a bath. It is, therefore, impossible to attribute the sensitizing effect to any intermediate oxidation of the dye.

"Experiments with various reagents such as potassium bromide, potassium dichromate, mercuric chloride, and dilute hydrogen peroxide seem to show that the chemical nature of the latent image produced by the less refrangible rays on the specially sensitized plates is precisely the same as that of the latent image produced by the more refrangible rays in the ordinary way.

"Further proof in the same direction is afforded by the fact that the effect of the sensitizers extends to the production of a visible effect by the prolonged action of light.

"The balance of evidence is therefore greatly in favor of the view that the dye absorbs the particular group of rays, and, in some way which is not at all clear, hands on the energy to the silver bromide, with which it is intimately associated, and which is thereby decomposed.

"For the present, for want of a better word, the phenomenon might be distinguished as *photo-catalysis*, and the sensitizer might be described as a *photo-catalytic* agent. As yet no connection can be traced between the chemical constitution and the general properties of a dye, and its sensitizing action."

With dyes that are bleached by light in the presence of air, it is the light which is absorbed by the dye in most cases which causes the bleaching. It is therefore probable, though not proved, that the optical sensitizers which are

not fast to light depolarize the silver bromide themselves or their decomposition products do. Of course it is necessary that these sensitizers shall dye silver bromide and it is possible, though also not proved, that the different behavior of the sensitizers with silver chloride and silver bromide in some cases is due to a difference in the adsorption of some dyes by the two halides.

In the bleach-out process we considered anethol as a special case of a chemical sensitizer for certain dyes in presence of air. If the anethol is oxidized, as we feel sure it must be, it would be legitimate to consider these same dyes as optical sensitizers for anethol in presence of air. Wager¹ has studied what seems to be a slightly different case, in which certain dyes act as optical sensitizers for the oxidation of iodide. "If strips of paper are soaked in solutions of the following dyes—methyl violet, methyl green, eosin, fuchsin, and fluorescein—and are then exposed to light and afterwards treated with a ten percent solution of potassium iodide, the iodine is liberated and the starch contained in the paper is colored blue or reddish blue, a strong reaction being obtained in all cases. Cyanin, on the other hand, although readily bleached by the light, does not give this reaction.

"Experiments made with narrow glass tubes lined with a thin layer of methyl violet and eosin show, on exposure to light, that, during the process of bleaching, oxygen is used up, but this is not the case with cyanin, which becomes completely bleached without any appreciable rise of water in the tube. In the case of methyl green and eosin, the absorption does not take place as rapidly and is not so pronounced as in the case of chlorophyll."

The cases studied by Wager are relatively simple because the reaction can be made to take place in two stages. It is quite certain that we have formed an oxidation product of the dye which oxidizes iodide to iodine. It is therefore not a splitting of oxygen, one half going to the dye and the other half to the iodide, though it would have looked like that if an amount of iodide equivalent to the dye had been added to the paper before the dye was bleached.

Of recent years some cases of optical sensitization have been studied which apparently cannot be included under the head of chemical depolarizers. A typical case is the effect of chlorine on the photochemical decomposition of ozone. Griffith and McKeown² point out that "the decomposition of ozone may be photosensitized by addition of chlorine, as shown by Weigert³ and recently investigated by Bonhöffer.⁴ The effective light in this case (in the region $\lambda = 416 \mu\mu$) is strongly absorbed by chlorine, but practically not at all by ozone. The reaction is zero-molecular with respect to ozone, and Bonhöffer has found that each quantum absorbed by the chlorine results in the decomposition of two molecules of ozone. Bromine also acts as a sensitizer, but here about thirty molecules of ozone are decomposed per quantum absorbed by the bromine."

¹ Proc. Roy. Soc., 87B, 397 (1914).

² Trans. Faraday Soc., 20, 598 (1925).

³ Z. Elektrochemie, 14, 591 (1908).

⁴ Z. Physik, 13, 94 (1923).

Bodenstein¹ has discussed this case more in detail. "We are familiar with several so-called sensitised reactions. These are reactions in the course of which a substance absorbs light without itself undergoing any change, while another substance, which is also present, undergoes a chemical reaction at the expense of the energy absorbed by the former. The oldest photochemical process, the foundation of our very existence, the growth of plants, is one of these "sensitised" reactions. A number of more transparent examples are now known, mainly as the result of Weigert's investigations.²

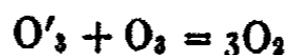
"The most thoroughly investigated of these is probably the decomposition of ozone sensitised by chlorine. Here chlorine absorbs the light without reacting itself, and for each quantum of this light two molecules of ozone are decomposed.³ This provides an extraordinarily simple kinetic equation:

$$-dO_3/dt = k.$$

"The decomposition of ozone, when plotted, shows a straight line which suddenly turns off horizontally the moment the ozone is used up.

"This process can of course only be explained by supposing that the chlorine molecule communicates its surplus energy to the ozone molecule, thereby causing its decomposition. It is of no concern how the communication of energy takes place. But the fact that the yield is quite independent of the ozone concentration shows that the chlorine molecule with its surplus energy collides often when the ozone concentration is small and less often when it is great, before it finds an ozone molecule to decompose. (The collisions may take place with chlorine itself or with oxygen.) This means either that it cannot communicate its energy at all except to an ozone molecule or that it can possibly communicate it to another chlorine molecule, which thus simply takes its place."

"A particularly interesting case of this communication of energy is shown by the dissociation of ozone. This process has been the subject of extensive experiments⁴ with ultra-violet as well as red light. The results were not very transparent. Now Dr. Kistiakowski has taken up the investigation again in my laboratory and has succeeded in showing that the contradictory results given in the older papers are due, to a very great extent, to an unsuitable interpretation of the experiments. His observations showed that the ozone molecules activated by the absorption of light must be divided into those that are decomposed with another ozone molecule according to the equation.



and those that communicate their energy to foreign molecules. These cause the reaction to be checked. But energy cannot thus be conferred in the same

¹ Trans. Faraday Soc., 20, 530 (1925).

² Weigert: Ann. Physik, 24, 234 (1907); Z. Electrochemie, 14, 591 (1908); Z. physik. Chem., 80, 103 (1912).

³ Bonhoeffer: Z. Physik, 13, 94 (1923).

⁴ Regener: Ann. Physik, (4) 20, 1033 (1906); v. Bahr: 33, 598 (1910); Weigert: Z. physik. Chem., 80, 78 (1912); Warburg: Ber. preuss. Akad. Wiss., 1913, 644; Griffith, Shutt, McWillie: J. Chem. Soc., 119, 1948 (1921); 123, 2752, 2767 (1923).

manner on all foreign molecules. The collisions possess the highest degree of elasticity in the case of helium and argon, a smaller degree in nitrogen, and the least in oxygen. Thus the kinetics of the photochemical decomposition of ozone bears a strong resemblance to the fluorescence of iodine and mercury vapour. The individual gases appear in a similar order in the case of the extinction of the fluorescence as when they receive energy from stimulated ozone molecules."

Allmand¹ has developed a chain mechanism for this case which pleases him very much. "One of the most remarkable facts in connection with certain photosensitised reactions in which a halogen is the absorbing component is the way in which the rate of reaction is independent of the concentration of the decomposing or reacting constituent. As examples may be mentioned the oxidation of CCl_2Br in CCl_4 solution by oxygen when sensitised by dissolved bromine,² and the photodecomposition of ozone in presence of bromine.³ The best-known case is the corresponding ozone-chlorine decomposition,⁴ which will be briefly considered in this paper. Here the reaction, in respect of ozone, is of zero⁵ order, and remains so until decomposition is complete within the limits of accuracy of measurement. So far as the writer is aware, there is no known case in which a non-absorbing component enters into a photochemical reaction with order other than between the limits 0-1, tending of course towards zero at high concentrations. But the example now under discussion seems rather too pronounced to be regarded simply as an extreme case of a general rule—one would certainly expect, judging from other instances, some indication in the experimental curve towards the end of the reaction of a change in order from zero to unity."

"The mechanism of ozone decomposition, under the conditions postulated, will be as follows:—(1) formation of activated Cl_2 molecules (Cl_2^*) by light absorption; (2) collision between Cl_2^* and O_3 molecules resulting in deozoneisation and energy degradation; (3) collision between Cl_2^* and O_2 molecules, resulting in the formation of activated O_2 molecules (O_2^*); (4) collision between O_2^* and O_3 molecules, resulting in deozoneisation and energy degradation. Other processes which will certainly occur are:—(5) spontaneous degradation of quantised energy held by Cl_2^* molecules, and (6) spontaneous degradation of quantised energy held by O_2^* molecules. Collisions between (7) O_2^* and O_2 molecules and between (8) Cl_2^* and Cl_2 molecules will be assumed to have as result, if any, simply the transfer of the quantised energy from one molecule to another of like kind,⁶ and hence not to change the composition of the system. Finally, as when a Cl_2^* molecule activates an O_3 molecule by collision, it is likely that the whole quantum is not transferred as such to the O_3 molecule, but rather that a portion of it is lost as low-grade radiation (*i.e.*, the

¹ Trans. Faraday Soc., 20, 603 (1925).

² Grüss: Z. Elektrochemie, 29, 144 (1923).

³ Bonhoeffer: Z. Physik, 13, 94 (1923).

⁴ Ann. Physik, 24, 243 (1907); Bonhoeffer: Z. Physik, 13, 94 (1923).

⁵ Not of first order, as stated by Norrish and Rideal.

⁶ Franck: Z. Physik, 9, 259 (1922).

quantum associated with an O_2 molecule is smaller than that associated with a Cl_2 molecule), it seems reasonable to assume that (9) a collision between an O_2 and a Cl_2 molecule will not result in Cl_2 formation."

"The mechanism here suggested appears to have two advantages over those proposed by Bonhoeffer¹ and by Weigert.² Firstly, it takes into account the deoxygenation of O_2 molecules by the O_2 molecules, which the work of Norrish and Rideal has shown to be, in all probability, formed under the conditions of the experiment; and secondly, it accounts for the course of the experimental curve, which other explanations fail to do. The assumptions involved in processes (7), (8) and (9), appear reasonable enough, whilst Bonhoeffer himself was forced (unwillingly) to conclude that the life of a Cl_2 molecule must be unusually long. Weigert's mechanism of "isochromatic fluorescence"³ enables him, of course, to avoid this conclusion."

There seems to be no question but that chlorine acts catalytically, in the sense that there is no permanent change in the chlorine during the reaction. Instead of starting from the Einstein hypothesis and inventing ingenious chain mechanisms which seem not to be susceptible of proof in the present state of our knowledge, one wonders whether it might not be wiser to start from the fact of a zero-order reaction and later to work out the quantum relations.

In order to have a zero-order reaction, the concentration of everything that counts must remain constant during the reaction. We get this, for instance, when hydrogen and chlorine react at constant pressure in presence of liquid water, because the hydrochloric acid is taken up by the water and consequently the concentration of the hydrogen and chlorine do not change. In the sensitization of the ozone decomposition by chlorine, the ozone concentration does change and therefore what we are measuring is not the rate of decomposition of ozone. The combined rates of activation and de-activation of chlorine must be slow relatively to the rate of decomposition of ozone by activated chlorine. This may prove to be an untenable hypothesis; but it should be considered.

It is clear that we have two classes of optical sensitizers, one which is merely a disguised chemical sensitizer and one, like the chlorine and ozone, where there is a transfer of energy in some way without any permanent

¹ Z. Physik, 13, 94 (1923).

² Z. physik. Chem., 106, 407 (1923).

³ The fact referred to early in this paper that the order according to which a non-absorbing component enters into a photochemical reaction always lies between 0-1, is of interest in connection with this conception of Weigert's. For, to take the case when all the incident light is absorbed, a photochemical reaction rate will then be represented by an equation of the type—

$$\text{Rate} = K(1 - e^{-kc}),$$

where c is the concentration of the non-absorbing component in question, and k a reaction velocity constant similar to k_1, k_2, k_3 above. k thus has, in any case, a formal resemblance to an ordinary radiation extinction coefficient, and of course must actually be such a magnitude if the Weigert conception holds. Whether an O_2 molecule is deoxygenated by collision with a "free" quantum or with one associated with a molecule such as Cl_2 or O_2 , naturally makes no difference to the type of equation which expresses the results.

change taking place in the sensitizer. We do not know how the transfer of energy takes place and we have no theory as yet as to what kind of substance will transfer energy in this or any similar way. A copper sulphate solution for instance absorbs certain wave-lengths very strongly. Will it act as an optical sensitizer for any reactions and, if so, for what reactions?

It is worth noting, however, that in all cases, no matter how involved, the law of Grotthuss holds that only the light which is absorbed is effective. A very interesting case of this is to be found with chlorophyll which shows a strong absorption band in the red, divided into two in the case of chlorophyll-*b*.¹ "The chief absorption is in the longer wave-lengths and is practically in the position of the maximum energy of the solar spectrum, during the greater part of the day. S. P. Langley's measurements of the position of maximum energy gave 650-666 $\mu\mu$ for high sun. The latter number is easy to remember, as Timiriazeff points out, being the 'number of the beast.' The middle of the chief band of chlorophyll-*a* is, in solution in ether, at 662 $\mu\mu$. In colloidal solution in one percent acetone, the band is shifted toward the red, so that its maximum is at 678 $\mu\mu$. This is the same as that of its natural state in the leaf. [According to Willstätter, chlorophyll probably exists in the leaf as an adsorption compound with a colloid, but not combined with a lipoid, as some have stated.] The maximum energy of solar radiation, also, would be for the greater part of the day nearer the red than the figure of Langley. Chlorophyll has a considerable absorption in the blue also, but practically none in the infra-red, nor in the yellow-green, and not much in the ultra-violet.

"It is remarkable that some of the earlier observers believed that the maximum photochemical change occurred in the yellow-green region, in which the absorption of light energy is minimal. This would be a difficulty in view of Grotthuss' law, and later observations, especially by Engelmann, showed it to be due to the incorrect estimation of the absorption of the screens used.

"A striking demonstration of the fact that the maximum evolution of oxygen is at the place of the greatest absorption of light was given by Engelmann.² This was done by the use of a bacterium, which was very sensitive to oxygen. Water containing these organisms was placed, along with a thread of a green alga, on the stage of a microscope. In the same plane, and along the thread of alga, a minute spectrum was projected by means of a spectroscopic arrangement beneath the stage. It was seen that the bacteria accumulated precisely at the places where the absorption bands of chlorophyll were situated.

"Another experiment showing the same fact, is due to Timiriazeff.³ A leaf on a plant is deprived of its stored starch by being kept in the dark. A small spectrum is projected on to its surface and, after some time, the leaf is decolorised by alcohol and treated with iodine. The absorption bands of chlorophyll are then found to be mapped out by the action of the iodine on

¹ Bayliss: "Principles of General Physiology," 562 (1915).

² Onderzoek. Physiol. Lab. Utrecht, 7, 191 (1882).

³ Proc. Roy. Soc., 72, 424 (1903).

the starch, which has only been formed in these places. Measurements have also been made, spectrophotometrically, of the absorption of light in different regions of the spectrum and compared with the photochemical effect. There are two maxima shown; but, when the curve is corrected for the normal spectrum, in which equal abscissas correspond to equal differences of wave-length, the second maximum in the blue end is found to be comparatively unimportant. . . . We may take it, then, that the maximal effect of the chlorophyll system is in relation to that part of the spectrum which is absorbed most."

Bayliss¹ calls attention to the fact that "the absorption of light by chlorophyll is such as to make the best use of the light available. But a green pigment is, of course, transparent to the green rays, which preponderate under water, so that it would be inefficient in that situation. Accordingly, as Engelmann² has pointed out, we find, in the seaweeds, red and brown pigments corresponding to chlorophyll and having the same function, but able to absorb effectively the green light available. For example, the red seaweeds show a maximum of carbon assimilation in the green and, spectrophotometrically measured, they show the greatest absorption in the same region, although there is also considerable absorption between the lines B and C, where the chief band of chlorophyll lies. The minimum of absorption is in the orange between C and D. This fact serves to illustrate the function of chlorophyll as an optical sensitizer; the same effect is produced by light of various wave-lengths, provided it is absorbed."

Eosin may change the wave-length of light necessary to kill bacteria.³ "Although ultra-violet light has so much more action on protoplasm than visible light has, it has been found by several observers that light which has no action by itself on infusoria, bacteria, or blood produces the effect of ultra-violet light when certain dyestuffs are present. Although the dyes used were, for the most part, fluorescent, this does not seem to be an essential factor. For a complete account of the work, the reader is referred to the monograph by Tappeiner and Iodlbauer.⁴ The general nature of the phenomenon will be clear from the few remarks following. Hertel⁵ exposed certain bacteria to light of 448 $\mu\mu$. This had no effect on them, either with or without the presence of eosin, 1 : 1200. Eosin has no absorption band in this position. Ultra-violet light of 280 $\mu\mu$ killed them in sixty seconds, without eosin. A third experiment consisted in taking light of 518 $\mu\mu$, that is, in the position of the absorption band of eosin, and making it of about the same energy as the ultra-violet light previously used. Alone, this light had no effect, as would be expected, since it has a longer wave-length than that found ineffective in the first experiment. On the other hand, in the presence of eosin, which has no action in itself, as the first experiment showed, the bacteria were

¹ "Principles of General Physiology," 567 (1915).

² *Onderzoek. Physiol. Lab. Utrecht*, 7, 209 (1882).

³ Bayliss: "Principles of General Physiology," 571 (1915).

⁴ "Die sensibilisierender Wirkung fluoreszierender Substanzen," (1907).

⁵ *Z. allgem. Physiol.*, 5, 95 (1905).

killed in seventy to ninety seconds. It appears that the action of the eosin is to be compared to that of an optical sensitizer."

Where it is possible for a substance to change color, the effect of colored light should be to change the substance to the same color as the light, provided there is no disturbing factor. This case has been realized by Wiener¹ with photochlorides. With the fulgides Stobbe² found³ that "orange light produces an orange dye and blue light a blue one. Thus, a substance is formed which does not absorb the light acting, so that no further change takes place; although if the product is exposed to light of a different wave-length from that under which it was produced, further change is effected since the light is absorbed." Bayliss has gone a bit beyond his facts. Blue light may have produced a blue dye; but the visible color was brown.

If we are dealing with a living organism, the reaction may be, and sometimes is, to produce a pigment, or more of a pigment, which will be complementary to the impinging light and which will keep the light from penetrating into the tissue. Light, which is absorbed by chlorophyll, tends to bleach the pigment but it also stimulates the formation of it.⁴ "There is evidence to show that, under the influence of light, the chlorophyll in a living cell is constantly being destroyed, but that under normal conditions the leaves remain green, the chlorophyll being reconstructed as fast as it is destroyed. Thus when leaves are exposed to a stronger light than usual, they become paler in colour, probably owing to the fact that under these conditions the chlorophyll is destroyed at a more rapid rate than it is reconstructed. This is frequently observed in the leaves of shade plants when exposed to bright sunlight, and is also observed in Algae such as *Spirogyra* which accumulate near the surface of water in the intense light of the sun during the summer months."

A more striking case is cited by Bayliss⁵ who seems to be a little puzzled by the formation of the complementary color, apparently not distinguishing between adaptation by a living organism and the normal elimination which we get with chemical compounds. "In certain cases, to which Engelmann⁶ has given the name of 'complementary chromatic adaptation,' we find that a pigment is actually formed under the action of coloured light and that the pigment has a colour which is complementary to that of the light to which the organism is exposed, so that this light is then absorbed. The alga, *Oscillaria sancta*, as shown by the work of Gaidukov,⁷ occurs in several colours between reddish purple and blue-green. If cultures are made, say, of the reddish-purple variety, we find that under red light a green pigment is produced. If we take the green variety; it becomes reddish under green light, brownish-

¹ Wied. Ann., 55, 225 (1895); Baur: Z. physik. Chem., 45, 613 (1903).

² Z. Elektrochemie, 14, 473 (1908).

³ Bayliss: "Principles of General Physiology," 568 (1915).

⁴ Wager: Proc. Roy. Soc., 87B, 387 (1914).

⁵ "Principles of General Physiology," 567 (1915).

⁶ Onderzoek. Physiol. Lab. Utrecht, 7, 209 (1882).

⁷ "Ueber den Einfluss farbigen Lichts auf die Färbung lebenden Oscillarien" (1902).

yellow under blue light, and so on. The work was done with great care and spectro-photometer curves of the various pigments were compared with those of the light under which they made their appearance."

These illustrations should be sufficient to prove the accuracy of the original postulates that only that light which is absorbed can be effective, and that all absorbed light tends to eliminate the substance absorbing it. It is entirely a question of chemistry whether any reaction takes place or what the reaction products are. I find that the silver salts bother some people unnecessarily, because the silver salts are moderately transparent while metallic silver is quite opaque. They overlook the fact that light is fairly efficient with silver salts in presence of a depolarizer, whereas it would be difficult to specify what reaction could take place between silver and gelatine.

We see that absorbed light may do one or more of three things. Under favorable conditions it may cause visible chemical change; under unfavorable conditions the absorbed energy may be converted completely into heat; under conditions which we cannot specify accurately at present a portion of the absorbed energy may appear as luminescence, either as fluorescence or as phosphorescence.

This last paragraph can be, and has been, said at much greater length if one speaks in terms of quanta. We will begin with a quotation from Bodenstein.¹ "To develop the kinetics of photochemical reactions let us analyse the process of light-absorption and its resulting effects. Nowadays we know that the absorption takes place in quanta; one molecule absorbs one quantum of energy. If the rays absorbed are visible or even ultra-violet, the energy thus conferred on the molecule is very considerable. It is of the order of the average energy of molecules at a temperature of some thousand degrees. Nevertheless in most cases the only result is the transformation of the energy into increased thermal motion. It is not sufficient to stimulate a chemical reaction.

"Yet, even if this is the case, every act of absorption need by no means be followed by a chemical reaction. Even then the molecule can communicate its increased energy to others in the shape of thermal motion, or again it can lose it by fluorescent radiation, or it can indeed employ the energy to effect a chemical reaction.

"As to the manner in which this occurs, the most obvious conception is that the energy is employed directly to sever an atom from the molecule; and this view has indeed often been taken.² But there are grave reasons against the conception. First, the energy that can be conferred on the molecule without effecting a severance is considerably greater than the work of dissociation.³ Secondly, radiation of energy as fluorescent light is possible, when the absorbing substance is a very dilute gas. This fact forces us to conclude that the molecule tends to radiate its surplus energy, in as far as it has no opportunity of communicating it as "flight"—energy to other molecules by collision

¹ Trans. Faraday Soc., 20, 526 (1925).

² Warburg: Sitzungsber. Akad. Wiss. Berlin, 1916, 324; 1918, 300.

³ Stern and Volmer: Z. wiss. Phot., 19, 275 (1920).

shortly after the act of absorption has taken place, or of accommodating itself to its increased energy during the collision by dissociation or some similar chemical reaction.

"This "competition" between fluorescence and communication of energy to other molecules has been observed in the vapours of iodine¹ and of mercury.² If the period between two collisions goes below the order of 10^{-8} sec., the fluorescence is extinguished more and more. Other observations have also given 10^{-8} secs. as the approximate term of life in the stimulated state.

"A similar competition between fluorescence and photochemical reaction has, so far as I know, not yet been observed. Photochemical processes have not yet been investigated at sufficiently low pressures. However, these investigations are soon to be expected, for they have been rendered urgent by the development of "dark reaction" kinetics.

"Up till now only such investigations have been made as could be carried out with high concentrations, *i.e.* short periods between two collisions. So here there can only be a question of competition between chemical reaction and communication of energy to other molecules. And here it has been found that in most cases the latter is quite inconsiderable."

It does not seem to me that Franck³ is much more helpful. "The researches of E. Warburg⁴ together with a great number of experiments of other workers carried out in recent years, have shown that the Einstein law of equivalence holds for primary photochemical reactions. By primary reaction is understood the first stage of a chemical reaction, for example the breaking down of a diatomic molecule into its component atoms. This occurs if the molecule has absorbed an amount $h\nu > D$, where D is the work of dissociation.

"Stern and Volmer⁵ were the first to show that from the physical standpoint the primary reaction is not the first elementary process, which consists rather in the excitation of a molecule, *e.g.*,



The conversion of excitation into chemical energy occurs only by collisions of the excited molecule with any other atom or molecule, provided that the collision takes place during the period of excitation. We have here a special case of a collision of the second kind. Otherwise the energy will be partly or wholly re-emitted by radiation in accordance with the Bohr frequency conditions, when we have the case of fluorescence instead of photochemical action.

"Indeed the experiments on gas fluorescence⁶ and on the excitation of molecular spectra by impacts of electrons,⁷ which are in many respects very

¹ Wood and Franck: *Physik. Z.*, 12, 81 (1911); Wood: 13, 353 (1912).

² Cario: *Z. Physik*, 10, 185 (1922); Stuart: 32, 262 (1925).

³ *Trans. Faraday Soc.*, 20, 536 (1925).

⁴ For literature see E. Warburg: "Naturwissenschaften" (1924).

⁵ Stern and Volmer: *Z. wiss. Phot.*, 19, 275 (1920).

⁶ For literature see P. Pringsheim: "Fluorescenz und Phosphorescenz."

⁷ For literature see J. Franck: *Physik. Z.*, (1918); or Foote and Mohler: "Origin of Spectra."

similar, show that at low pressure a molecule may take up many times its dissociation energy without dissociating. For example iodine can absorb and re-emit as a resonance spectrum an amount of energy five times the work of dissociation, when illuminated by the line $\lambda 1849$.¹ From the position of the longest wave-length member of the resonance series we can deduce that here at the maximum half the energy of dissociation can remain in the form of nuclear oscillations. A further example is to be found in the hydrogen molecule which, on excitation by electron collision, can emit as molecular spectrum four to five times the amount of the dissociation energy. If we consider also the experiments on the excitation of X-rays spectra which, due to secondary effects such as expulsion of electrons, are not so easy to interpret, we may arrive at values of the excitation energy which may exceed the work of dissociation a thousand times without leading to dissociation by a primary process."

"The well-known explanation of this effect is that the excitation energy is primarily employed in raising the electron to a higher quantum state, while the oscillation and rotation energies are only altered by the coupling of their periods with those of the electron system. It is, indeed, possible in hetero-polar molecules for the oscillation and rotation energies to change by light absorption without simultaneous changes of quantum number of the electron system, but the energy of such changes is so small compared with that of dissociation that it may be neglected.

"Consequently the question whether a photochemical dissociation is possible in one elementary act, that is without collision with molecules which chemically take no part in the reaction, is reduced to a consideration of the magnitude of the oscillation and rotation energy changes, which are coupled with the changes which the electron system undergoes on absorption of light. Only when this amount equals or exceeds D for the state considered can dissociation take place. We will deal later with the question of into what parts the molecule can dissociate. We must first consider whether and under what conditions we can give large quantities of rotation and oscillation energy to the molecule.

"Lenz has developed a theory which is concerned with the coupling of the electron with the molecular frequencies, and concludes that the rotation quantum number can only change by ± 1 , on the occasion of an electron jump.² We may therefore neglect the influence of rotation. He has also shown how the alteration in oscillation quantum number may be understood by reference to the correspondence principle.³

"We can consider this question more qualitatively but more generally. We may assume that, when light is absorbed, the nuclei can only alter their potential energy, as the raising of the electron system to another quantum state alters the strength of the chemical binding of the molecule. This change

¹ O. Oldenberg: *Z. Physik*, 18, 1 (1923).

² Lenz: *Physik. Z.*, 21, 691 (1920).

³ Lenz: *Z. Physik*, 25, 299 (1924).

may be large or small, positive or negative. A schematic diagram of the potential energy of the nuclei, u , as a function of their distance apart, r , allows us to review the possible cases more easily."

"Before we proceed to show that the observations agree with our expectations, we must discuss into what parts the molecule can break down on absorption of light, which is the same question as what parts of the molecule are oscillating relative to one another in the relevant excited state.

"In heteropolar molecules we know that in the normal state of the electron system, positive and negative ions are oscillating, and if we consider such a molecule to be disrupted by an adiabatic process, we shall have a dissociation into a positive and a negative ion. In a higher quantum state, where an electron of the positive ion is raised to a higher quantum orbit, the binding will be stronger, and we can expect no dissociation by absorption of light. Whether we can remove an electron by radiation from the anion will remain uncertain so long as an electron affinity spectrum is unknown. In any case it is a matter not of excitation, but of the complete removal of an electron, and as the binding will of course be very weak we shall have a dissociation into a positive ion, an electron and a neutral atom. The result is sufficient for us that an adiabatic separation of the molecule on excitation into its component atoms is not possible. A fuller discussion of the excitation of the band spectra of heteropolar molecules will be found in a recent paper by Mulliken.¹

"We know at present very little also about the binding of homopolar molecules. We have two possibilities to discuss.

"The first and simpler of the two is that in which the atoms of the molecule are bound together by the van der Waals forces. As Debye² has shown, free atoms in the act of collision may polarise each other, or so arrange their existing moments, that an attraction ensues. If the same process takes place in these molecules the orbits will be disturbed; but the quantum numbers of the electron system will be preserved in the molecule. Such molecules can be adiabatically disrupted into normal atoms, and in the case where the atoms are of the same kind, the work of dissociation will be of the order of magnitude of the atomic heat of vaporisation.

"When such a molecule is excited by light, the electron of one of the atoms will be raised to a higher quantum orbit, and with weak bindings the wavelengths associated with such transitions will be almost identical with those emitted by the free atoms. In fact, all very loosely bound compounds like Na_2 and Hg_2 show such a relation, and the bands attach themselves closely to the atom lines.

"In the mercury molecule not only the lines due to the transitions $1.5\text{S}-2\text{p}_2$ and $1.5\text{S}-2\text{P}$ exist (as can be seen from the fact that the bands attach themselves to these absorption lines) together with further atom lines which are found accompanied in emission by bands, but also the metastable states

¹ Mulliken: *Phys. Rev.*, 26, 1 (1925).

² Debye: *Physik. Z.*, 21, 178 (1920).

of the atom are metastable in the molecule.¹ Plainly these facts are related with the smallness of the work of dissociation, which is of the order of 1 kilocalorie. In absorption these bands are found on the long wave-length side of the absorption lines, which shows, as mentioned above, that the binding is stronger in the excited state. Attached to these unresolvable bands are continuous spectra stretching in the long wave-length direction over a wide region. From this we may conclude that not only the oscillation energy existing in the initial state can be used to raise the electron system to a higher quantum state, but that also the kinetic energy of two impacting free atoms can be called into service.² Expressing this in the form of an equation we obtain:—

$$\text{Kin. relative energy of atoms} + (\text{heat of dissociation})\text{Hg}_2 \\ + h\nu = (\text{Energy of excitation})\text{Hg}_2$$

“Here we may have then a photochemical elementary act in which two colliding atoms, by the influence of light absorption, unite in an excited molecule, in the manner to be expected from Diagram III.³

“Conversely, we should have in molecules in which the potential energy of the nuclei follows the relations shown in Diagram I^a, the possibility that the molecule may take up so much oscillation energy through absorption that it parts into a normal and an excited atom.

“Of course such a process is only possible in a molecule which is capable of separating adiabatically into these components, and it appears that the halogen molecules belong to this class. Accordingly they should belong, certainly in the excited and probably also in the normal state, to the type of molecule bound together by van der Waals forces, and indeed their relatively small work of dissociation is in complete agreement with this view.”

“If our assumptions are correct, an accurate analysis of the terms of the halogen spectra would naturally lead to very accurate values of the work of dissociation of the halogen molecules, from purely spectroscopic data.

“Dymond, working in my Institute, has, in a paper shortly to be published, given further reasons why light of a wave-length covered by the continuous absorption spectrum can bring about dissociation of iodine. The principal argument is that we are forced to conclude that the emission of series of resonance lines on illumination with a series of wave-lengths, from long waves to the neighbourhood of $\lambda 5000$, consists of molecular fluorescence.

“Wave-lengths shorter than $\lambda 5000$ give no trace of fluorescence, although they are more strongly absorbed than in the region of band absorption. He also describes a luminescence due to recombination of normal atoms with those in the metastable state. That the transition $2p_2 - 2p_1$, may take place

¹ From this we can explain the long afterglow of the molecular fluorescence of mercury, first noticed by Philips (Proc. Roy. Soc., 89A, 39 (1924)) and also the fact that the luminescence is only emitted by the influence of collisions. See Franck and Grotrian: Z. Physik, 4, 89 (1921).

² Born and Franck (Z. Physik, 31, 411 (1925)) maintain that in this case only unstable quasi-molecules can be formed. This limitation is not necessary for molecules which are built up by normal atoms bound together by the van der-Waals forces.

³[Not given in this report.]

spontaneously in the molecule although forbidden in the atom is to be explained from the strong electrical disturbances of the atoms of the molecule on each other. The work of dissociation, and therefore the electrical disturbances, are here much greater than in the mercury molecule.

"In conclusion we must mention the second possible type of homopolar molecule and a few arguments for its existence.

"In this class the electron system of the atom is not only disturbed but quite new orbits of the electrons appear which belong to totally different types of motion from those of the free atoms. As an example, let us take the assumption frequently made that two or more electrons are common to both atoms of a diatomic molecule; the orbits cross in some way and encircle both nuclei. Such molecules can certainly not separate from the normal state adiabatically into two atoms, and the electron jumps associated with the formation and dissociation of these molecules cannot be produced by radiation processes but only through the energy of collisions. Here we should expect a considerably greater value for the dissociation energy, as indeed is the case in nitrogen and oxygen.

"Recently Blackett and the author, in a paper shortly to be published, have more closely examined the hydrogen molecule. No point of convergence of bands has been observed in the molecular spectrum of hydrogen. Together with other reasons we can take this as indicating the impossibility of adiabatic separation of the atoms.

"Through the influence of collisions, which as is known can cause transitions of the electron orbits between different classes of mechanical orbits, it has been shown in the paper mentioned that the hydrogen molecule can dissociate into a normal and an excited atom. An adiabatic separation is possible as soon as a transition of the electron system into that of the atom has occurred through the collision process."

Ornstein¹ says that "in the photochemical process excited molecules are formed by light, collisions transform the energy absorbed by the quantum absorption into chemical energy; in the second stage newly formed molecules lose their energy by way of emission."

Roy² states that "molecular collisions have no place in unimolecular reactions. 'Activation' is a preliminary process of 'loosening of the chemical bonds' between the two components of a molecule and may result from absorption of radiation (endothermic reaction) or emission of radiation (exothermic reaction) according to whether it is necessary for the binding electrons to move to higher or lower quantum states to render the molecules reactive. A molecule, presumably, passes through a series of quantised states by absorption or emission of some definite frequencies before coming to a final 'reactive' state. A 'reactive' molecule subsequently undergoes decomposition by absorption of radiation of all frequencies greater than a certain limiting value. For the steady continuance of the reaction it is necessary that the

¹ Trans. Faraday Soc., 20, 505 (1925).

² Trans. Faraday Soc., 20, 523 (1925).

process of 'activation' must run at a rate sufficient to furnish the number of 'reactive' molecules necessary for the reaction. A satisfactory law of uni-molecular reactions can easily be worked out¹ on the basis of these ideas."

Kautsky² has discussed chemiluminescence. "Haber and Zisch³ have investigated the luminescence caused by the combination of sodium vapour with chlorine and have explained it theoretically. My colleague Dr. Zoher and I⁴ gave independently a similar explanation for the extraordinary bright chemiluminescence which is caused by the oxidation of silikone at room temperature. (Silikone is a yellow solid substance, a mixture of siloxen ($\text{Si}_2\text{O}_2\text{H}_2$) and several coloured reaction products of siloxen.) This explanation may be expressed briefly in the following way. The energy which is set free in any chemical reaction remains first associated with the reaction products. In the simplest case of chemiluminescence the reaction product itself may give off its energy, or at least a part of it, in the form of radiation. In other cases we may first have a transfer of energy without radiation from the reaction products on neighbouring molecules. These molecules may be molecules which take part in the reaction or molecules of another kind. By this transfer of energy, they are transformed into an unstable active modification, richer in energy, and light is emitted when they return to their normal states.

"Chemiluminescence is therefore the reversal of a photochemical or a sensitised photochemical reaction. Here the absorption of light causes directly a chemical reaction or, in the case of sensitisation, it causes a chemical reaction in consequence of a transfer of energy on neighbouring molecules⁵. Chemiluminescence only differs from fluorescence in so far as the activation is of a different kind. In the case of chemiluminescence it is the energy of a chemical reaction which causes the radiation, in the case of fluorescence it is the absorbed light which has the same effect.

"It therefore ought to be possible to force a substance which shows fluorescence to give chemiluminescence by using suitable reactions for activating its molecules. We might expect then that the spectrum of chemiluminescence would be identical with the spectrum of fluorescence. Experiments were therefore made to force fluorescent dyestuffs like rhodamine and rhodamine sulphonate to give chemiluminescence. In order to attach this end the following conditions have to be fulfilled. We need a reaction which gives the energy necessary to activate the dyestuffs and which does not change their emission of light. We further need conditions in order that the transfer of energy from the place of reaction to the molecules of the dyestuffs is thorough and effective. These conditions are fulfilled by some solid colourless derivatives of silicon, for instance silico-oxalic acid siloxen and some colourless oxidation

¹ Roy: Proc. Roy. Soc., 110A, 543 (1926); Z. Physik, 34, 499 (1925).

² Trans. Faraday Soc., 20, 591 (1925).

³ Haber and Zisch: Z. Physik, 9, 302 (1922).

⁴ Kautsky and Zoher: Z. Physik, 9, 267 (1922); Z. Electrochemie, 29, 308 (1923); Naturwissenschaften, 11, 194 (1923).

⁵ The correlation between chemiluminescence, sensitisation and photochemical reactions has been investigated by Kautsky and Thiele: Z. anorg. Chem., 144, 197 (1925).

products of siloxen.¹ These latter derivatives of silicon have a strange morphological structure.² They are built up of lamellae consisting of layers of molecules only one or two molecules thick. These layers lie over one another like the leaves of a book. They adsorb basic dyestuffs in water solution. The adsorption compounds are strongly coloured and show fluorescence. The lamellae themselves may be oxidized by adding small amounts of potassium permanganate in acid solution without showing luminescence and without change in their morphological structure. The energy of this oxidation is easily transferred to the dyestuff molecules since they are adsorbed on the lamellae. They are, therefore, in the direct neighbourhood of the places of reaction.

"The chemiluminescence which is caused by adding a solution of permanganate to these adsorption compounds is surprisingly bright. The same chemiluminescence is found if these adsorption compounds, in a dry state, are oxidised with ozone. This shows that it is the adsorbed dyestuff which causes the chemiluminescence. The dyestuffs were made to fluoresce by illuminating them with ultra-violet light. There was no difference between the fluorescent spectra of the adsorption compounds and of the dyestuffs in solution.

"The above-mentioned theory was verified quantitatively in so far as the chemiluminescent spectra of rhodamine and rhodamine sulphonate were found to be identical with their fluorescent spectra."

Lindemann³ considers that there were two totally different problems in the discussion before the Faraday Society. "The one set of problems is connected with the secondary effects following upon photochemical activation. Here we have a long, often complicated, chain of reactions, whose investigation is more a matter for the chemist than the physicist at the present stage.

"By contrast the primary reaction seems to me to be comparatively simple and in good accord with Einstein's law, the so-called deviations being due to a misapprehension of what is claimed. When one quantum of light is absorbed by an atom it moves the electron from one stationary orbit to another stationary orbit, or ionises it completely, as in the photo-electric effect. The excited atom can give up its store of energy in various ways, either by the return of the electron to the primary orbit with emission of radiation, as occurs in the phenomena of fluorescence or phosphorescence, or by the transfer of the energy to kinetic energy of some atom with which it collides (*Stoss zweiter Art*), or by taking part in some chemical process. Einstein claimed that every atom must be photochemically affected. His law merely gives the maximum number which can take part in the primary reaction. The chance of a photochemical reaction taking place depends upon the excess of the energy of the quantum over the energy of activation. Thus the efficiency of the light will in general increase as the frequency is increased,

¹ Kautsky: *Z. anorg. Chem.*, 117, 209 (1921).

² Kautsky and Hersberg: *Z. anorg. Chem.*, 147, 81 (1925).

³ *Trans. Faraday Soc.*, 20, 607 (1925).

and may have any value between 100 percent and 0 percent as the long wave limit is approached."

I do not myself believe that it is possible, as Lindemann and others assume, to keep an electron long enough in an outer orbit to give rise to chemiluminescence. If this cannot be done, we must recognize that there are two types of fluorescence, as indeed there are. The cathode ray fluorescence of mercuric bromide, cadmium sulphate, and lead sulphate involves the actual decomposition of these salts into mercury and bromide, cadmium oxide and sulphur trioxide, and lead and sulphate radical respectively; but nobody would guess it from the discussion, and consequently I, for one, do not feel inclined to accept at their face value the views which I have just quoted at some length. I should like to see a little more definite knowledge.

Having acquired a fairly definite idea of the general principles governing photochemical change, we can finish up the nominal subject of this report in short order, because the theory of the displacement of equilibrium by light is quite simple.¹ If we expose a system to a given light of given intensity, the light which is absorbed will tend to eliminate the substance absorbing it and will do so if the conditions are favorable. We will suppose that x grams of the absorbing substance would be changed in the first second if there were no disturbing factors. The two disturbing factors are the reverse reaction in the dark and the reverse reaction due to the absorption of light by the photochemical conversion products. If we postulate that these two reverse reactions produce y and z grams respectively of the original substance in the first second, the total conversion in the first second will be $x - y - z$ grams. Theoretically, we can eliminate the reverse photochemical change by using only the wave-lengths which decompose the original substance. In this case the amount of conversion in the first second will be $x - y$ grams and will be zero when $x = y$. In other words, the favorable condition for getting a marked displacement of equilibrium is that the reverse reaction shall be very slow. The monomeric form of nitrogen peroxide has a very strong band in the more refrangible end of the spectrum; but it would probably be impossible to produce a perceptible bleaching by the blue light because the reverse reaction is too rapid. Ozone is formed photochemically from oxygen by some of the wave-lengths less than 200μ and is decomposed photochemically by some of the wave-lengths² longer than 200μ . Since we have no ray filter which will let through the wave-lengths shorter than 300μ while cutting off those longer than 300μ , the amount of ozone formed in the first second by any given light is $x - y - z$ grams. Since the temperature coefficient of the reaction in the dark is usually much greater than the temperature coefficients of the photochemical reactions, we can usually decrease y relatively to $x - y$ or to x by lowering the temperature. This is actually the case with ozone. At low temperatures we can get a fairly good yield of ozone, while there is practically no ozone formed at 200° because the decomposition is so rapid.

¹ Cf. Sheppard: Chem. Rev., 4, 319 (1927).

² For decomposition of ozone by red light, see Kistiakowsky: Z. physik. Chem., 117, 337 (1925).

Violet light converts the ordinary dissolved sulphur¹, S_{λ} , into the insoluble sulphur, S_{μ} . The amount of conversion decreases with rising temperature because the speed of the reverse reaction in the dark increases. Wigand was only able to get a lowering of the freezing-point of sulphur of a few tenths of a degree by exposure to light; but it is possible that one could do better than this because Wigand did not use the most favorable wave-lengths.

Water is a mixture of compounds having the general formula $(H_2O)_n$. Some of them must absorb some rays in the ultra-violet more strongly than the other modifications do, in which case it should be possible, theoretically, to displace the freezing-point of water. Whether one can get a measurable displacement depends on the rate of the reverse reaction. One could undoubtedly get results with some of the aldoximes.

Similarly it is possible, theoretically, to displace the inversion temperature for the red and yellow mercuric iodides; but there are no data to show whether the displacement would be measured in degrees or in thousandths of a degree. Dey² finds that the orange-yellow $(HgS)_2 \cdot HgI_2$ turns black on exposure to sunlight and reverts in the dark. One factor in making possible the decomposition of mercurous chloride into mercury and mercuric chloride is that the reverse reaction takes place slowly in the dark. Sasaki³ reports that light displaces the equilibrium between ferrous salt and iodine towards the iodide side.

Coehn and Becker⁴ have studied the effect of light on mixtures of sulphur dioxide and oxygen. The effective light does not exceed $265\mu\mu$ in wave-length, which makes it practically impossible to use uviol glass and actually there is almost no effect in uviol glass. Equilibrium was reached from both sides in presence of ultra-violet. With a quartz mercury lamp as source of light the photochemical equilibrium is at about 65% conversion at 160° , as against 100% conversion for thermal equilibrium in presence of a catalyst. Coehn and Becker say that the photochemical equilibrium is practically independent of the temperature up to 800° , where the thermal conversion in presence of a catalyst is only about 30%. With a ratio of $SO_2 : O_2 = 1 : 13$ they obtained a conversion of 80% at 800° as against a catalytic one of 44%.

Over this whole range of temperature the rate of conversion or decomposition is practically zero in the dark in absence of a catalyst. The reverse reaction, y , in the dark therefore drops out practically completely in these experiments, as Coehn and Becker themselves state. Since the rate at which equilibrium is reached in the light increases enormously between 160° and 800° with a temperature coefficient of 1.2, the only way in which a displacement of equilibrium can be avoided is by postulating that one is measuring the antagonistic action of two groups of wave-lengths, just as we know we do in the ozone formation. The effects of both sets of wave-lengths must increase proportionally with the temperature.

¹ Rankin: J. Phys. Chem., 11, 1 (1907); Wigand: Z. physik. Chem., 65, 442 (1909); 77, 423 (1911).

² Nature, 112, 240 (1923).

³ Z. anorg. Chem., 122, 61 (1922).

⁴ Z. physik. Chem., 70, 88 (1910).

Instead of adopting this obvious explanation, Coehn and Becker assume that there cannot be antagonistic groups of wave-lengths in this case, that probably there are not in any case, and that, consequently, the ozone work is wrong. They ignore the fact that their position is unsound theoretically and that it does not account for their own experimental observation that the photochemical equilibrium is not displaced appreciably by change of temperature although the rate of reaction is.

In the Cornell laboratory we have obtained a conversion of only about 25% at a little under 200°, passing a Tesla oscillatory discharge through the gas, which probably gives us a different group of wave-lengths in the ultra-violet. This is not inconsistent with Coehn and Becker's experiments; but is quite inconsistent with their assumptions.

Chapman, Chadwick and Ramsbottom¹ have shown that dry carbon dioxide at atmospheric pressure is decomposed 2.5-3.0 percent by ultraviolet light, while at 36 mm pressure 46 percent of the carbon dioxide is decomposed. The main reaction is, of course, $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$; but some of the oxygen is converted into ozone. When moist carbon dioxide is used, there is practically no decomposition at all. Ellis and Wells consider that under these conditions "the catalyst (moisture) exerts a marked influence in determining the mode of distribution of energy among the molecules of the reacting substances (the two oxides of carbon and oxygen)." This sounds well, but do we know that water vapor does act as a catalyst at these temperatures? It is quite as possible that the water vapor acts as a screen. The experiment should be repeated with concentric tubes and the water vapor in the outer one. Then we should have something definite to go on.

Coehn and Sieper² have also studied the action of ultra-violet light on carbon dioxide. The wave-length of the active rays lies below $254\mu\mu$. When the pressure is such that the dry gas is decomposed to the extent of 18 percent, the merest trace of moisture reduces the amount of decomposition to 0.1 percent. Neither formic acid nor formaldehyde is formed and the water undergoes no change. Coehn and Tramm³ find that presence of water vapor has no apparent effect on the rate of combination of carbon monoxide and oxygen under the influence of ultra-violet light. This looks as though the water vapor acted merely as a screen.

The photochemical formation of phosgene has been studied by Bodenstein⁴. "The chlorine used contained 0.08 per cent oxygen and a trace of water. Carbon monoxide was made by the reaction of sulfuric acid and formic acid, and was freed from oxygen, carbon dioxide, and water. The results with various mixtures of carbon monoxide and chlorine are very complicated, and are influenced by the moisture present. Experiments on

¹ J. Chem. Soc., 89, 22 (1896); 91, 942 (1907); Ellis and Wells: "The Chemical Action of Ultraviolet Rays," 111 (1925).

² Z. physik. Chem., 91, 347 (1916).

³ Ber., 54, 1148 (1921).

⁴ Rec. Trav. chim., 41, 585 (1922); Ellis and Wells: "The Chemical Action of Ultraviolet Rays," 113 (1925).

the relation between the radiations absorbed and the amount of material transformed show that oxygen retards the reaction and exercises a rather constant effect until just at the end, when its effect is suddenly diminished. Oxygen is sensitized by irradiated chlorine. Carbon dioxide formation is, other things being equal, proportional to the carbon monoxide pressure, increases with the chlorine pressure, but more slowly than directly proportional to it, and decreases with increasing oxygen concentration, but not so rapidly as to be inversely proportional to it. The sensitized reaction also shows a large Draper effect.

"Coehn and Becker¹ find that when carbonyl chloride is passed through a quartz tube at the ordinary temperature, and at the same time submitted to the action of rays from a quartz mercury lamp, it is partly decomposed into carbon monoxide and chlorine. When 1 cc of carbonyl chloride is passed through the quartz tube (20 centimeters long and 0.5 centimeters in diameter) per minute, the amount of decomposition is 3.3-4 percent. The effect is chiefly due to the short ultraviolet rays, since the use of tubes of uviol glass, which are transparent only to waves of greater wave-length than $265\mu\mu$ resulted in a degree of decomposition of only 0.46-0.5 per cent. In ordinary glass tubes there is no decomposition. Coehn and Becker remark that in all the cases hitherto, namely, the photochemical equilibria of sulfur trioxide, hydrogen chloride, and carbonyl chloride, the actual equilibrium is affected only by ultraviolet rays. Rays of greater wave length simply act catalytically on the attainment of equilibrium. Wherly² reports that while experiments using ultraviolet for the production of phosgene by the union of carbon dioxide and chlorine have been successfully tried, the disadvantages on a commercial scale are manifest. By far the greater proportion of phosgene is manufactured by passing carbon monoxide and chlorine over platinized asbestos, charcoal or boneblack heated to redness."

The influence of light on the gaseous systems, hydriodic acid, hydrobromic acid, hydrochloric acid, and their components has been investigated by Coehn and Stuckardt³ at room temperature, equilibrium being reached from both sides. The experiments were carried out in quartz glass, uviol glass, and Jena glass. The percentage decomposition of the three acids at equilibrium is as follows:

| | Quartz Glass | Uviol Glass | Jena Glass |
|-------------------|--------------|--------------|--------------|
| | 220 $\mu\mu$ | 254 $\mu\mu$ | 300 $\mu\mu$ |
| Hydriodic acid | 92 | 100 | 100 |
| Hydrobromic acid | 100 | 20 | 0 |
| Hydrochloric acid | 0.4 | 0 | 0 |

Hydrochloric acid requires ultra-violet light of $220\mu\mu$ for decomposition and even then the rate of change is small. Under similar conditions hydro-

¹ Ber., 43, 130 (1910).

² Color Trade J., 8, (1918).

³ Z. physik. Chem., 91, 722 (1916); Ellis and Wells: "The Chemical Action of Ultraviolet Rays," 110 (1925).

bromic acid is decomposed rapidly and completely. Hydriodic acid is decomposed by blue and violet light.

The displacement of the hydrogen-oxygen equilibrium by ultra-violet light or by radium is complicated by the possible formation of ozone or hydrogen peroxide. Dickinson¹ found that "hydrogen and oxygen in contact with mercury combine to form water at 45°C or even at room temperature when illuminated by rays from a quartz mercury arc lamp cooled by a blast of air. This is said to be due to dissociation of the hydrogen molecule by collisions with mercury atoms excited by absorption of the mercury line, 253.7 μ . In absence of any one of the three substances or of the exciting radiation, no reaction takes place." This seems to be a very clear-cut case of an optical sensitizer.

"The equilibrium point of hydrogen chloride in the dark lies practically at the point of complete formation of this compound from its elements. This equilibrium can be brought about in the absence of light by submitting the mixture of hydrogen and chlorine to the catalytic action of charcoal. Coehn and Wassiljewa² find that, if pure hydrogen chloride is submitted to the action of ultraviolet rays from a quartz mercury lamp, it is split up to such an extent that, on collecting the gases over a solution of potassium iodide, about two cubic centimeters of hydrogen are produced in a quarter of an hour. The hydrogen chloride was passed through a quartz tube, which was at a distance of about two centimeters from the lamp, the tubing through which the gases were led away from the quartz tube being protected from all light. When the quartz tube was replaced by one made of ordinary glass, or of uviol glass, no decomposition of the hydrogen chloride took place."

When a solution of anthracene is exposed to light, the anthracene polymerizes to dianthracene³, which may or may not crystallize, depending on the concentration. When melted, dianthracene goes back completely to anthracene and it also goes back more slowly at lower temperatures in contact with the solution. This has been studied exclusively⁴, so far as I know, as the balancing of a light reaction against a dark reaction; but of course there must be light of some wave-length which will accelerate the depolymerization of the dianthracene. Luther and Weigert say that the absorption of light by dianthracene solutions is negligible in comparison with that of anthracene solutions; but this has no special significance because it is a question of the absorption of single bands and the statement cannot be true for the dianthracene absorption bands.

Luther⁵ has studied the reversible decomposition of the silver halides by light electrometrically and has shown that the electrical effect of each in-

¹Proc. Nat. Acad. Sci., 10, 409 (1924); Ellis and Wells: "Chemical Action of Ultraviolet Rays," 101 (1925).

²Ber., 42, 3183 (1909).

³Orndorff and Cameron: Am. Chem. J., 17, 658 (1853).

⁴Luther and Weigert: Z. physik. Chem., 51, 297; 53, 385 (1905); Byk: Z. Elektrochemie, 14, 460 (1908).

⁵Z. physik. Chem., 30, 628 (1899).

tensity of light can be duplicated in the dark by a suitable concentration of the halogen in question.

Haldane¹ found that when air containing as much as one percent of carbon monoxide is shaken with blood solution in bright sunlight, no pink color at all could be observed in the solution; yet, when the bottle was taken into the dark, the pink color appeared at once on shaking. This was confirmed by Hartridge² who gives the following data for the displacement of equilibrium caused by light:

| Percentage Carbon Monoxide Haemoglobin | | | | | |
|----------------------------------------|----|----------------|----|--------------|----|
| Dark | 96 | Dark | 92 | Dark | 91 |
| Sunlight | 42 | Electric light | 88 | Daylight | 80 |
| Sunlight | 35 | Sunlight | 40 | 6" Magnesium | 64 |

Hartridge says that it is almost self-evident that the active rays correspond to one or more of the absorption bands. "Four little glass tubes containing the same mixture of COHb and ferricyanide were therefore placed in a spectrum projected by a diffraction grating and Nernst lamp; one was placed in the position of each band. On examination, it was found that the solution placed in the ultra violet had changed to methaemoglobin, the other solutions remaining practically unchanged. This showed clearly that the ultra violet rays had been responsible for the action on the COHb and explains the value obtained in the first experiment quoted for the dissociation caused by different light sources. Those sources rich in actinic rays, *i.e.* sunlight, magnesium, etc., cause a big dissociation, while electric light, lamp light, etc., cause very little because of their poorness in these rays."

In a later paper Hartridge and Roughton³ worked with such a mixture of haemoglobin, oxygen, and carbon monoxide, that there was no free haemoglobin. In one experiment at about 0°, the equilibrium was so displaced by light to the oxygen that there was less than one percent carbon monoxide haemoglobin in the light and well over sixty percent when equilibrium was reached in the dark. Curiously enough, oxyhaemoglobin is apparently insensitive to light so far as dissociation is concerned.

Dewar and Jones⁴ have studied the decomposition of liquid iron carbonyl, Fe(CO)₅ by visible light. When dissolved in dry ether or petroleum ether, light causes decomposition to carbon monoxide and to so-called solid iron carbonyl, Fe₂(CO)₉, which separates as reddish-orange hexagonal plates. These crystals are practically insoluble in ether, petroleum ether, and benzene; but are slightly soluble in methylal, acetone, and alcohol, and are much more soluble in pyridine, forming a reddish solution. When liquid iron carbonyl is dissolved in pyridine and exposed to light, the solution gives off carbon monoxide and turns red, but no solid iron carbonyl precipitates unless the solution is very concentrated. This is, of course, what one would expect.

¹ J. Physiology, 20, 504 (1896).

² J. Physiology, 44, 22 (1912).

³ Proc. Roy. Soc., 94B, 336 (1923).

⁴ Proc. Roy. Soc., 76A, 558 (1905); 79A, 68 (1907).

In the light, the iron carbonyl decomposes even against a pressure of 100 atmospheres of carbon monoxide. The reverse reaction takes place very slowly in the dark but goes on even at low pressures.

"The velocity of the reverse reaction, $\text{Fe}_2(\text{CO})_9 + \text{CO} = 2\text{Fe}(\text{CO})_5$, which proceeds in the dark, was studied by using the same tubes that we used for the examination of the direct reaction. The results show that this is an extremely slow reaction at the ordinary temperature. Tube E, above, containing petroleum ether, has a pressure of three atmospheres after three months, so that only 73 percent of the gas had been absorbed by the solid; after eleven months the pressure was still 1.68 atmospheres, so that 92 percent of the products had recombined.

"In line with this is the fact that dissolved, liquid, iron carbonyl decomposes in the light even against a carbon monoxide pressure of one hundred atmospheres, while the reverse reaction takes place in the dark, even at low pressures, though very slowly.

"In order to determine what kind of light was most effective in inducing this decomposition, small tubes containing a ten percent solution of iron pentacarbonyl in ether were exposed in different parts of a solar spectrum and also to sunlight under different coloured screens. It was found that most rapid decomposition occurred in the blue, then green, closely followed by yellow, and lastly red: exposure under red glass produced roughly about one-tenth the amount of solid produced under blue glass in the same time. Exposure of the liquid in quartz tubes to the electric arc causes slow decomposition only, and the acetylene flame is still less active." It is not quite clear why the red light should produce the least decomposition. It is probably a question of effectiveness rather than of absorption.

Solutions of liquid iron carbonyl in nickel carbonyl "are of a much paler yellow colour than solutions of equal concentrations in other solvents. Thus, for example, a ten percent solution of iron carbonyl in ether has just the same intensity of colour as a thirty percent solution in nickel carbonyl. A ten percent solution deposits no solid after exposure to bright sunlight for several weeks; a twenty-five percent solution (by volume) deposits no solid from the liquid, but solid is deposited in the vapour space above the liquid; a fifty percent solution deposits some solid both in the liquid and in the vapour space.

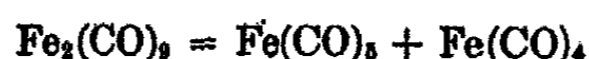
"That no more decomposition occurs in dilute solutions of iron carbonyl in nickel carbonyl is shown by the facts that no gas is evolved from these solutions, and that solid iron carbonyl is only sparingly soluble in nickel carbonyl. The absence of any change is not to be accounted for by the absorption of the active light by the nickel carbonyl, since the iron carbonyl has been shown above to be sensitive to light in the visible part of the spectrum which is not absorbed by nickel carbonyl. This fact was further confirmed by exposing a small tube full of iron carbonyl immersed in liquid nickel carbonyl to light, when decomposition was found to take place rapidly."

Dewar accounts for this by assuming the formation of $\text{FeNi}(\text{CO})_9$, analogous to $\text{Fe}_2(\text{CO})_9$. "A compound of this kind, though unstable in itself

(since the vapour above the solutions contains iron carbonyl and the concentrated solutions deposit some solid), may yet be unacted upon by light. The existence of this compound is rendered probable by the fact that solutions of iron carbonyl in nickel carbonyl have such a pale colour compared to solutions of the same concentration in other solvents."

"When solid iron carbonyl is heated alone, no change takes place below 100°C; at this temperature a solid and a *green* liquid are formed. But if the solid be heated with liquids such as ether, petroleum ether, or toluene, change begins at about 50°C, the solid decomposes and the liquid acquires an intense green colour. The intensity of the green colour is so great that the solutions are almost opaque, even in thin layers; in more dilute solutions the absorption spectrum shows a distinct band in the yellow. These green solutions, on exposure to light, again deposit yellow crystals of the solid carbonyl, and become colourless."

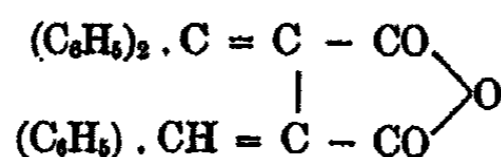
The green compound appears to be iron tetracarbonyl, FeCO_4 , or some polymer of this. The decomposition of diferro-nonacarbonyl in presence of solvents such as toluene and ether is probably to be represented by the equation



"Further evidence in support of this was obtained by carrying out the decomposition in tubes filled with carbon dioxide and fitted with a mercury manometer. No change of pressure was produced by the decomposition. On exposing the tubes, after heating and now containing a green solution, to light, the orange crystals of diferro-monacarbonyl were deposited, showing that during the action of heat iron pentacarbonyl had been formed." The decomposition of iron tetracarbonyl on heating corresponds apparently to the equation



Stobbe¹ has shown that the orange-yellow crystalline powder of triphenylfulgide (A-form), for which he writes the formula



is stable in the dark but changes when exposed to sunlight or to arc light to a light-brown mass which consists at least in part of the B-form (formula not given). If one uses blue and violet rays instead of white light, the product is dark brown and is probably more nearly pure B-form. The B-form goes back slowly in the dark and more rapidly when exposed to red and yellow light to the orange-yellow A-form.

Stobbe² has also studied the effect of light of different wave-lengths on styrene, the cinnamic acids, etc. "The polymerization of styrene, which takes place spontaneously in the dark, can be accelerated considerably by

¹ Z. Elektrochemie, 14, 474 (1908).

² Z. angew. Chem., 35, 587 (1922); Ber., 58B, 2415 (1925).

exposure to sunlight or to the light of the mercury lamp. A hard, glassy mass is obtained, which swells and then dissolves slowly in styrene, benzene, toluene, nitrobenzene, or carbon tetrachloride. On addition of alcohol to any of these solutions there is obtained a precipitate, which is at first slimy but becomes brittle after repeated precipitation of pure metastyrol, a poly-molecular, saturated hydrocarbon, $(C_7H_8)_x$. The glassy mass, which used to be considered as pure metastyrene is a solid solution of the polymer in amounts of monomeric styrene running up to 25%. Pure metastyrene is not obtained by polymerization in the light (or by the other polymerization methods) because there is also a depolymerization under the influence of light. A benzene solution of metastyrene, after exposure to sunlight, contains unsaturated styrene, as can easily be shown. The pure, white, easily powdered, metastyrene changes to the glassy, yellow product on exposure to ultra-violet light. There is therefore an equilibrium $x(C_7H_8) \rightleftharpoons (C_7H_8)_x$, in sunlight, just as there is for the isomerization of the nitrobenzaldehydobenzoins and for the stereomerization of the different ethylene derivatives by ultra-violet light as studied by Stoermer.

"Like styrene, p-methoxystyrene, $CH_3OH \cdot C_6H_4 \cdot CH : CH_2$, is converted by sunlight into a polymer $(C_8H_{10}O)_x$ very similar to metastyrene. No polymerization occurs when the monomeric ether is illuminated by the quartz mercury lamp, and the polymerized methoxystyrene is completely depolymerized by the same wave-lengths. The equilibrium $x C_8H_{10} \rightleftharpoons (C_8H_{10})_x$ is therefore very dependent on the wave-length, more of the polymer being formed with longer wave-lengths and more of the monomer with shorter wave-lengths."

Stilbene¹ changes in sunlight to the distilbene (tetraphenyl cyclobutane). The unsaturated monomeric stilbene absorbs the longer ultra-violet rays and is therefore polymerized by sunlight, while the distilbene at the same concentration absorbs only the shorter ultra-violet rays and consequently is depolymerized by the light from the quartz mercury lamp. It is possible to displace the equilibrium very much in either direction by a suitable choice of wave-length.

Rice² finds that "the yellow methyl and ethyl esters of benzoylacrylic acid are transformed in the sunlight into the corresponding stereoisomeric colorless esters. The reverse transformation of the colorless into the yellow esters take place if the former are exposed to the sunlight in solutions containing a trace of iodine or bromine. In a similar manner the yellow methyl and ethyl esters of p-methoxybenzoylacrylic acid on exposure to the sunlight in benzene solution are transformed into the corresponding colorless isomeric esters. The reverse transformation of the colorless into the yellow esters again results when solutions of the colorless solids containing a crystal of iodine are exposed to the sunlight. The yellow methyl and ethyl esters of

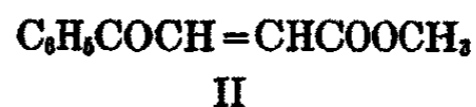
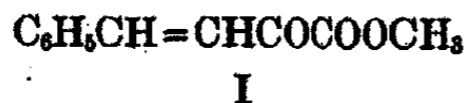
¹Stobbe: *Z. angew. Chem.*, 35, 578 (1922).

²J. Am. Chem. Soc., 45, 222 (1923); 46, 214, 2319 (1924); Ellis and Wells: "The Chemical Action of Ultraviolet Rays," 176 (1925).

p-ethoxy-benzoylacrylic acid isomerize when exposed to the sunlight both as solids and in benzene solution. The unstable, colorless esters thus formed are transformed quantitatively both in the dark and in the sunlight, when in benzene solutions containing a crystal of iodine, into the stable yellow isomers. Hydrochloric acid brings about the same change."

"According to Reimer¹ the products formed by the action of sunlight on methyl benzalpyruvate exposed in the dry condition are a polymeric ester, melting at 154°C., obtained in small quantity, and an oil, probably a mixture of isomers and decomposition products. On exposure in benzene solution, a reaction which in other cases almost invariably gives an isomeric compound, the product of reaction was found to be a polymer, melting at 117°C. Reactions with these two polymeric substances have shown that the higher melting has the structure of the truxillic acid series, while the lower melting one is related to the truxinic acids. The formation of the latter compound may be explained on the assumption that in solution isomerization had taken place and that the isomeric ester had polymerized. The reaction is an unusual one as but few cases of polymerization of this type of substance in solution have been described.²

"A comparison of this ester, I, with that of benzoylacrylic acid, II,



is of interest. The system of 'conjugated double linkages' in the two is the same but stands in a different relation to the phenyl and the carboxyl groups. The products obtained from I are polymers, while on exposure of II to the sunlight no polymers are formed but isomerization takes place with the greatest ease. Whether the difference in reaction of these two substances is due to difference in the chemical effect of the neighboring groups on the unsaturated part of the molecule or to a difference in the physical state of the compounds during exposure is still to be determined.

"When specimens of cinnamic acid, melting point 42°, obtained from the acids, melting points 68° and 58°, are exposed to bright daylight during two years, the resulting product consisted of unchanged acid and β-truxillic acid³; but when samples having the melting points 42°, 58°, and 68° were exposed in quartz tubes to direct sunlight which was sufficiently powerful to cause temporary fusion, with consequent isomerization, the product consisted chiefly of α-truxillic acid with little β-truxillic acid and small quantities of trans-cinnamic acid and benzoic acid. The light reactions of cis- and trans-cinnamic acid have been further studied by Stobbe and Steinberger⁴. They find, as did de Jong,⁵ that exposure of cis-cinnamic acid to sunlight gives

¹ J. Am. Chem. Soc., 46, 783 (1924).

² See Ciamician and Silber: Ber., 42, 1388 (1909); Stobbe and Rücker: Ber., 44, 869 (1911); Reimer and Kelly: Am. Chem. J., 50, 157 (1913).

³ Stobbe: Ber., 52B, 666 (1919).

⁴ Stobbe: Ber., 55B, 2225 (1922); Chem. Abs., 17, 549 (1923).

⁵ Chem. Abs., 16, 2683 (1922).

besides the expected β -truxinic acid trans-cinnamic acid and α -truxillic acid. Exposure for 96 hours of the liquid melt of cis-cinnamic acid to the rays of a quartz-mercury lamp produced extensive isomerization into trans-cinnamic acid, but neither β -truxinic nor α -truxillic is formed, the melt thus behaving like benzene or methyl alcohol solutions. It may be said in general that irradiation of the cinnamic acids in the liquid state (solution or melt) produces isomerization but no polymerization. The chief action is ascribed to rays from 270 to 320 μ although the shorter and the longer rays are also not without influence

"The isomerization reaction proceeds in the same way in both the mercury arc rays and in sunlight, but the yield of dimers is very different. Taking each day of exposure as equal to seven hours, cis-cinnamic acid after 200 hours in the mercury arc ray gives 4.4 per cent dimers, and after 196 hours in the sunlight 71.0 per cent. For trans-cinnamic acid the values are 2 per cent after 364 hours in the mercury arc ray and 85.7 per cent after 161 hours in the sunlight. Long ultra-violet rays favor polymerization, while the shorter rays hinder it, and exert a depolymerizing action on the truxinic and truxillic acids. Comparison of these sunlight experiments with those of de Jong¹ and of Stoermer² shows that cis-cinnamic acid yields β -truxinic acid always, and generally in predominant amount, but that, especially on long illumination, there is also isomerization into trans-cinnamic acid, and subsequent polymerization to α -truxillic acid. Trans-cinnamic acid, on the other hand, is almost exclusively polymerized to α -truxillic acid; only on long illumination are there formed relatively small amounts of β -truxinic acid, accompanied by considerable resinification.

"Experiments with mixtures of equal parts of cis- and trans-cinnamic acids show that the trans-cinnamic acid mixed with the cis- form produces no increase of β -truxinic, and that therefore, contrary to de Jong's belief, α -truxinic acid is formed only from two molecules of cis-cinnamic acid. In agreement with Stoermer and Scholtz³, Stobbe and Steinberger conclude that β -truxinic acid has a meso and not a racemic structure. Experiments by Stobbe and Lehfeldt have shown that the β -arylacrylic acids, including trans-cinnamic acid, are dimerized and autoxidized to benzaldehyde, both in the solid state and in aqueous suspension. Both processes are accelerated by a few drops of hydrochloric acid, the oxidation to a greater extent than the dimerization, and on long illumination the yield of α -truxillic acid diminishes and that of benzaldehyde increases. Cis-cinnamic acid behaves similarly, the yield of β -truxinic acid on long irradiation, especially in the presence of hydrochloric acid, decreasing as the result of the autoxidation of the cis-cinnamic acid. Here, too, the formation of β -truxinic acid is independent of the presence of admixed trans-cinnamic acid; both isomers polymerize, independently, to their dimers, even in suspension.

¹ Chem. Abs., 6, 2746 (1912).

² Chem. Abs., 14, 58 (1920).

³ Chem. Abs., 15, 1888 (1921).

"When the acid freshly prepared from the sodium salt of trans-cinnamic acid is illuminated in sunlight in hydrochloric acid suspension, it unexpectedly yields only β -truxinic acid and no α -truxillic acid.

"In connection with the stereoisomers of substituted ethylene Stoermer¹ states that the conversion of the labile into the stable modification by the action of light, particularly in the presence of a halogen, is not uncommon. The converse change, produced by light alone, has been remarked in very few cases. Perkin has noted the conversion of methylcoumarinic acid into methylcoumaric acid by sunlight, but Stoermer finds that in the coumaric acid series the tendency is the other way, the stable form changing to the labile under the influence of ultra-violet rays. Thus Perkin's change occurs only to the extent of 25 per cent, whereas coumaric acid yields 75 per cent of coumarin, methylcoumaric acid yields 75 per cent of methylcoumarinic acid, ethylcoumaric acid yields ethylcoumarinic acid quantitatively, and acetylcoumaric acid is also quantitatively changed to acetylcoumarinic acid. That the changes are caused by the ultra-violet rays is proved by means of light filters, the interposition of a filter which absorbs ultra-violet between the lamp and the solution preventing any change of the stable to the labile modification. Hence the less fusible stable forms of stereoisomeric compounds can be changed directly, under definite conditions, into the more reactive labile modifications if energy is supplied by ultraviolet rays. Thus the stable form of *o*-anisylcinnamic acid, which could not be changed into the labile modification by Stoermer and Frederici has been converted to the extent of 50 per cent by using a more intense radiation. In the case of stereoisomeric α -alkylated acids, the conversion of the stable into the labile form is a matter of great difficulty. The case of cinnamic acid is interesting. A benzene solution of ordinary cinnamic acid was exposed for eight days to the light of a uviol lamp, with the result that 25-30 per cent of Liebermann's isocinnamic acid, melting point 58° , was produced. Allocinnamic acid in benzene is converted into ordinary cinnamic acid under similar conditions. Also fumaric acid changes to maleic acid in eight days, but the conversion of mesaconic acid into citraconic acid is very difficult, these being α -methylated acids. When stilbene in benzene is exposed to ultraviolet for eight days, it is converted to the extent of about 90 per cent into isostilbene, which can be reconverted into stilbene by heating at 170° - 180° for one hour, by the vapor of fuming nitric acid in a few minutes, and quantitatively by the exposure to sunlight of its solution in carbon disulfide containing a trace of bromine.

"According to Stoermer, Frederici, Brautigam and Neckel² the stable, less fusible forms of the following compounds are transformed into the labile or more fusible stereoisomers when their benzene or alcoholic solutions are exposed to the action of the ultraviolet rays from a uviol lamp for several days; coumaric acid 75; methylcoumaric acid 75; ethylcoumaric acid over

¹ Ber., 42, 4865 (1909); J. Chem. Soc., 98II, 114 (1910).

² Ber. 44, 637 (1911).

90; propylcoumaric acid 85; methylcoumaramide, 50; ethylcoumaramide 100, propylcoumaramide 95; methyl coumarate; coumarin acetylcoumaric acid over 90; methyl benzoylcoumarate; methyl-*o*-nitro-*o*-methoxycinnamate 80; *o*-nitro-*o* methoxycoumaric acid 40, *p*-methoxycinnamic acid 25; sodium-*o*-chlorocinnamate 10; piperonylacrylic acid 17; maleic acid; *o*-anisylcinnamic acid 35-40; *o*-anisylcinnamide 70; *o*-anisylcinnam-methylamide 36; and the corresponding ethylamide 40; β -*o*-anisyl- α -methylcinnamic acid 5, and the corresponding amide 5; cinnamic isocinnamic acid, melting point 42°, 30-40; phenyl tolyl ketoxime, 40; phenyl anisyl ketoxime. In most cases the reaction is a balanced one, and the number given for each compound represents the percentage for the less fusible compound which has been transformed when equilibrium is established. Crotonic acid is not transformed to any appreciable extent.

"The method is recommended as a suitable one for the preparation of allo-stereoisomers in several cases and also for the detection of spatial isomerism between a pair of compounds. In a few instances the addition of methyl and ethyl alcohol to the unsaturated compounds occurs during the exposure to the ultraviolet but the amounts of such products are usually small. It is suggested that the transformation and the percentage amount transformed depend on the energy differences between the stereoisomers. Sodium fumarate is not transformed, although the corresponding acid yields 30 per cent of maleic acid. These investigations also state that *o*-chlorocinnamic acid, or its sodium salt, when exposed to ultraviolet rays is partly transformed into the allo-acid, $C_9H_7O_2Cl$, but when glacial acetic solutions are used, part of the acid combines with acetic acid, giving a product, $C_{11}H_{11}O_4Cl$, melting point 212°-213°. When a solution of mesaconic acid is subjected to the action of ultraviolet, water or methyl alcohol appears to combine with the acid. The change from one stereoisomeric form into another under the influence of radiation is frequently observed in the case of compounds containing an ethenoid linkage. In some instances ultraviolet rays produce changes which are the converse of this brought about by ordinary light."

Heilbron and Wilson¹ have shown that "cinnamaldehyde-semicarbazone exhibits a type of phototropy which is the converse of that ordinarily observed. When first prepared, it is colorless, and, if immediately placed in the dark, undergoes no change of color. If, however, the semi-carbazone is exposed to diffused sunlight for some hours, although no visible effect is noticeable, on now placing it in the dark, a yellow color develops on the exposed surfaces, which again disappears on reexposure to light. This phenomenon, which is designated as *reversed* photography, has been further studied by Heilbron, Hudson and Huish².

"The methoxycinnamaldehyde-semicarbazones and -phenylsemicarbazones all crystallize from solution as colorless substances, and, with the exception of *m*-methoxycinnamaldehyde-diphenylsemicarbazone which is

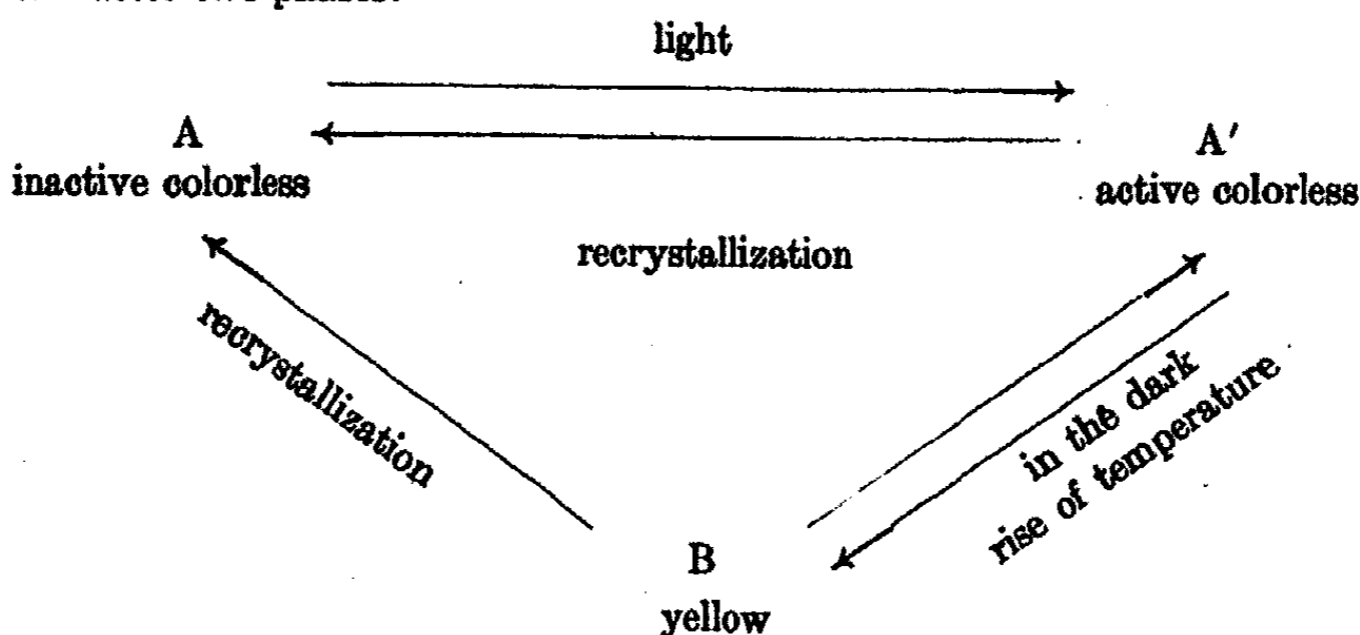
¹ J. Chem. Soc. 105, 2892 (1914); Ellis and Wells: "The Chemical Action of Ultraviolet Rays," 130 (1925).

² J. Chem. Soc. 123, 2273 (1923).

insensitive to either sunlight or ultraviolet, all exhibit reversed phototropic properties. On the other hand, the thiosemicarbazone derivatives, which may be expected to be quite similar in character, exhibit only *direct* phototropy, becoming yellow in diffused sunlight and not reverting to the colorless modification on removal from the source of light. A series of experiments has been carried out with the view of obtaining evidence of phototropic change in solution, and for this purpose solutions of the intensely phototropic *o*-methoxycinnam-aldehyde-thiosemicarbazone in various solvents were exposed for lengthy periods to sunlight. In no case, however, was there the slightest indication of the production of any color in the solution and it may thus be reasonably concluded that phototropy is essentially a characteristic of the solid state.

"The phenomenon of thermotropy is very strikingly manifested by the semicarbazones exhibiting reversed phototropy. So long as any of these remains unactivated by light, rise in temperature produces no color change. On the other hand, after exposure to sunlight, in certain cases even for so short a period as five minutes, the colorless activated substance becomes yellow almost immediately when placed in a steam-oven.

"It will be seen that in a reversed phototropic change the first effect must be one involving the absorption of a certain number of energy quanta, whereby the molecule is transformed from its inactive, colorless phase (A) into an *active* colorless variety (A'). This latter form is in turn transformed into the colored modification (B), phototropic equilibrium being established between the latter two phases:



Stobbe has shown that in the case of the fulgides¹ the active wave-lengths involved in the bringing about of *direct* phototropic change are those which the substance itself absorbs. As indicated below, this applies equally in the present series. An ordinary photographic plate was fixed, washed, and, when almost dry, dusted over with colorless, inactive cinnamaldehyde-semicarbazone. The plate was then placed in the spectrograph and exposed for about two hours, an iron arc being used as source of radiation. On examining the semi-carbazone, no visible change was detected, but after leaving the plate

¹ J. Chem. Soc., 123, 2273 (1923).

over night, a narrow, yellow band was clearly indicated at $280 \mu\mu$, this being the characteristic ultraviolet frequency of the substance.

"In order to determine whether energy is emitted during the transformation in the dark of the active, colorless into the colored form, a photographic plate covered with cinnamaldehyde-phenylsemicarbazone was activated in strong light and then placed in the dark in contact with an undeveloped plate. After being left over night, during which time the phenylsemicarbazone had become yellow, the upper plate was developed, but no mark whatsoever could be detected on it.

"Heilbron, Hudson and Huish believe that a phototropic change simply represents an intermediate stage of an irreversible chemical reaction. The active phases of higher energy content which are similar to Baly's activated molecules¹ would tend either to lose energy and again pass into the inactive phase (recrystallization effect), or, on the other hand, to undergo complete chemical change with formation of a new substance. Thus Stobbe² has found with the fulgides, that, when the phototropic change is frequently repeated, the difference of color between the two forms becomes gradually less, the phototropic process giving place to a non-reversible chemical reaction in which a substance of different constitution is produced. Similarly, Halban and Geigel³ have shown that, in the case of tetrabenzoyl ethylene, an irreversible chemical change rapidly follows the primary phototropic process.

"The phototrophy of other substances has also been studied by Stobbe.⁴ The zone of stimulation for colorless β -tetrachloro- α -ketonaphthalene lies in the ultraviolet, while the reverse change is caused by yellowish-green or yellowish rays. Red and blue rays have no action.⁵

"Phenylbenzylidenehydrazine, which forms light yellow crystals or a white powder, becomes red on exposure to violet or ultraviolet rays, becoming again colorless when exposed to yellow or green light. Phenylanisylidene- and phenylcuminyldenehydrazines behave in the same manner, as do also osazones of the benzil series.⁶ Tetraphenyldihydrotriazine⁷ and ethyl oxaliso-butyrates⁸ have also been observed to exhibit phototropy."

Kailan⁹ has determined the equilibrium which exists between fumaric and maleic acids and also the velocity of transformation in either direction. "The transformation was carried out in aqueous solutions of the acids of 0.084 N and these were subjected to the action of a quartz-mercury lamp in vessels of glass and of quartz. In the solid condition fumaric acid is not converted into maleic acid by ultraviolet, while maleic acid is converted into fumaric acid only to the very slightest extent. In aqueous solution whether the solu-

¹ Phil. Mag., 40, 15 (1920).

² Loc. cit.

³ Z. physik. Chem., 96, 233 (1920).

⁴ Loc. cit.

⁵ See also Stobbe: Ber. Verhandl. K. Sächs Ges. Wiss. Leipzig, 74, 161 (1922); Chem. Abs., 17, 2030 (1923).

⁶ Bilts and Wienands: J. Chem. Soc., 76, 910 (1899).

⁷ Walther: J. Chem. Soc., 84I, 592 (1903).

⁸ Wislicenus and Liesewetter: J. Chem. Soc., 74I, 240 (1898).

⁹ Z. physik. Chem., 87, 333 (1914); Ellis and Wells: "The Chemical Action of Ultraviolet Rays," 174 (1925).

tion was contained in glass or in quartz vessels, an equilibrium between the two acids could be reached from either side. The equilibrium was displaced somewhat toward the maleic acid side with increasing concentration. Thus at 45°-50° with N/10 solution the equilibrium mixture contained 75 per cent of maleic acid and in 4N/10 solution 79 per cent of maleic acid. The velocity of transformation was much greater in quartz vessels than in glass vessels, while the position of the equilibrium is uninfluenced. Maleic acid is formed when a mixture of benzoic and formic acids is exposed either to the action of ultraviolet or to the penetrating radium rays.¹ Formic acid is decomposed by the action of radiation from a quartz-mercury vapor lamp, and benzoic acid is converted into formic acid in the same manner."

A detailed study of the photolysis of acetaldehyde has been made by Berthelot and Gaudechon,² who state that "ultraviolet rays of long wave-length do not convert the aldehyde into acetic acid in the absence of oxygen. Under the influence of medium and extreme rays oxidation takes place even in the absence of oxygen, a portion of the aldehyde being converted into acetic acid. The amount of acid produced is far greater when the aldehyde is in the form of vapor than when it is liquid. With rays of wave-length 250 $\mu\mu$ polymerization is rapid, both para and meta acetaldehyde being formed. No resinification results from the action of long ultraviolet rays, and it is only slowly produced by the medium and extreme rays. The presence of water checks polymerization and resinification, but favors acidification, formic acid being produced in this case and in amount almost equal to that of the acetic acid. Of three compounds studied, viz.: acetaldehyde, ethyl alcohol, and acetic acid,³ only acetaldehyde is decomposed by sunlight (wave-length greater than 300 $\mu\mu$). Rays from a mercury lamp screened by thin glass which absorbs all rays of wave-length less than 300 $\mu\mu$ decompose acetaldehyde in accordance with the equation $\text{CH}_3 \cdot \text{CHO} = \text{CO} + \text{CH}_4$. Frequently the proportion of methane to carbon monoxide actually found is somewhat less than corresponds to this equation, for the light causes polymerization of some of the aldehyde to paraldehyde which is then photolyzed to carbon monoxide and ethane or more complex substances. These latter reactions are most readily produced by the extreme ultraviolet rays. Direct rays from a mercury lamp, without any interposed screen, photolyze not only acetaldehyde but ethyl alcohol and acetic acid. Ethyl alcohol is decomposed primarily into acetaldehyde and hydrogen,⁴ but usually some carbon monoxide and ethane are formed by the further decomposition of the aldehyde. By the photolysis of acetic acid a gas was obtained which contained 44 per cent of carbon dioxide, 17 per cent of carbon monoxide and 39 per cent of combustible gases.⁵ These results relate to photolysis in absence of air. In presence of water the reactions take substantially the same course, but there is a tendency toward the formation of acid products."

¹ Kalan: Monatsheft, 41, 305 (1920); Chem. Abs., 15, 1100 (1921).

² Compt. rend., 156, 233 (1913); Ellis and Wells: "The Chemical Action of Ultraviolet Rays," 155 (1925).

³ Compt. rend., 156, 68 (1913).

⁴ J. Soc. Chem. Ind., 30, 1086 (1911).

⁵ J. Soc. Chem. Ind., 29, 1081 (1910).

Luther and Plotnikow¹ point out that quite a number of photochemical reactions, which people have called reversible, are not so in fact. A simple case of this is the iron oxalate developer, which probably few people can remember having used. "The red solution of ferrous oxalate becomes muddy and then green on standing in the dark, because the ferrous oxalate is oxidized to ferric oxalate by the oxygen of the air. If this green solution is exposed to a sufficiently intense light, it becomes red again because the light converts ferric oxalate into ferrous oxalate and carbon dioxide. If one only considers the color change, one might put this in the class of truly reversible reactions. This is of course not the case because the reversible reaction is necessarily tied up with an irreversible one, the oxidation of oxalic acid by the oxygen of the air. The color change from red to green and back again cannot be repeated indefinitely. It will stop as soon as either the oxygen or the oxalic acid is used up. Some years ago Dr. Kuntze-Fechner, working in this laboratory, found that with a number of the so-called phototropic solids the apparently reversible color change was accompanied by an irreversible formation of a stable isomer." This actually occurs with the triphenylfulgide² to which reference has already been made. The orange and brown modifications are identical in composition and give the same thing when dissolved. They differ only in the solid state. If the phototropic change is repeated frequently, the difference between the shades of the two forms becomes less, owing to the occurrence of a chemical change which results finally in the complete conversion of the fulgide into a new substance, the photo-anhydride.

Many people do not like to say there has been a displacement of equilibrium by a catalyst when alcohol decomposes to acetaldehyde and hydrogen with nickel and to ethylene and water with alumina, because the second reaction is possibly not reversible. We could get round this by postulating that the nature of the catalyst determines the nature of the change from one stationary state to other stationary states.

Following this line of thought, I should like to mention a few cases which do not at present constitute a displacement of equilibrium in the strict sense of the word. Berthelot and Gaudechon³ found that ultraviolet light causes partial polymerization of acetylene to a yellow solid, presumably the same that the newspapers made so much of an outcry over when Coolidge obtained it by the action of his improved cathode ray tube. Under similar exposure ethylene polymerizes to a liquid boiling above 100°. A mixture of ethylene and acetylene gave a mixture of the polymerization products and no interaction between ethylene and acetylene.

Acrylic acid⁴ in a sealed glass tube is apparently not affected appreciably by diffused light. Sunlight converts it slowly into a solid polymer. When sealed in a quartz tube and exposed to ultraviolet light, it polymerizes rapidly to the same solid.

¹ *Z. physik. Chem.*, 61, 513 (1908).

² *Stobbe: Ann.*, 359, 4 (1908).

³ *Compt. rend.*, 150, 1169 (1910).

⁴ *Moureu, Murat and Tampier: Ann. Chim.*, (9) 15, 231 (1921).

Quite extraordinary are the polymerization products¹ of vinyl chloride, $\text{CH}_2\text{:CHCl}$, and vinyl bromide, $\text{CH}_2\text{:CHBr}$. "The chloride forms an amorphous, insoluble substance of specific gravity 1.406, which melts above 130°C . with decomposition.² The polymerized bromide is likewise insoluble in water, alcohol or ether, and has a specific gravity of 2.075. The polymer begins to decompose at $125^\circ\text{--}130^\circ\text{C}$. It is stated by Plotnikov³ that a solution of vinyl chloride, as distinguished from ethylene, polymerizes to a substance thought to be $(\text{CH}_2\text{:CHCl})_n$ in the extreme ultraviolet of a mercury lamp. Sunlight is effective only in the presence of catalyzers, such as the salts of manganese, cobalt, nickel, copper and vanadium, and is most active with uranyl salts. The white precipitate obtained dissolves in many organic solvents to form colloidal solutions varying in character from paste to solid. Details of the production of useful products by the polymerization of vinyl esters when employing the mercury vapor lamp are given by Klatt and Tollett.⁴ The polymerization can be accelerated by catalyzers, benzoyl peroxide, ozonides, and anhydrides of organic acids in conjunction with an agent giving off oxygen (perborates, percarbonates, silver oxide, etc., being mentioned for the purpose).

"The polymerization products, which form more or less rapidly in accordance with the intensity of illumination and the temperature, are solid, colorless, and transparent celluloid-like masses which are odorless and can be turned, cut, planed, and otherwise manipulated to form various articles. These solids rendered plastic in hot water can be molded and, upon cooling, the material becomes hard again. Chlorinated esters may be polymerized by heat and light as a two-stage operation in the following manner: 1 kilogram of vinyl chloroacetate is mixed with from 0.5 to 1 gram of benzoyl peroxide and carefully heated in a large vessel provided with a reflux condenser. At from 60° to 100° polymerization takes place, while the temperature rises rapidly. At this time care should be taken to cool the reaction vessel. The violence of the reaction may be modified by diluting the reaction liquid with an indifferent solvent; for instance, in the present example, about 300 grams of chlorobenzene can be used. The reaction product is a viscous syrupy mass which can be further treated by exposing to light without a diluent, solid masses being obtained as the remaining unaltered vinyl ester polymerizes. The syrupy solution or a solution made from the completely polymerized ester may be used as a lacquer or other coating compound. When allowed to dry in thin layers, colorless films of a celluloid-like nature are said to be obtained. Vinyl chloride may be polymerized by ultraviolet rays, but the product derived is not as satisfactory as that obtained from the esters mentioned. According to Kuhl⁵ the polymerization of vinyl esters (vinyl acetate or vinyl chloroacetate) by ultraviolet light yields solid masses, which may serve as substitutes for celluloid and which are fireproof and odorless. The poly-

¹ Ellis and Wells: "The Chemical Action of Ultraviolet Rays," 146 (1925).

² Baumann: *Ann.*, 163, 317.

³ *Z. wiss. Phot.*, 21, 117 (1922).

⁴ U. S. Patent 1, 241, 728, Oct. 2 (1917).

⁵ Reports of the Progress of Applied Chemistry issued by the Society of Chemical Industry, 1, 192 (1916); *J. Soc. Chem. Ind.*, 34, 623 (1915).

merization is assisted by catalytic agents (organic peroxides) to give thick syrups which on illumination give solid masses having valuable properties.

"The polymerization of vinyl chloride in the extreme ultraviolet has been utilized by Plotnikow¹ to make "synthetic rubber." He exposed a 2.5 per cent solution of vinyl chloride in methyl alcohol to ultraviolet radiation. Carbon tetrachloride was found to accelerate the transformation.

"As a representative of the β - γ , ethylenic acids, γ phenylvinylacetic acid in benzene solution was exposed to ultraviolet rays by Stoermer and Stockmann.² The acid resinified to a considerable degree. Although the allo-form could not be obtained in crystalline form, the crystalline allo-amide was isolated and converted by raying into the stable variety. Ostromuiskenski³ obtained by the polymerization of vinyl bromide a material which he termed caouprene bromide. This exists in three forms, α , β , and γ . When the α and β forms are submitted to the action of ultraviolet the γ form is yielded. Stobbe and Toepfer⁴ report that p-vinylanisole is polymerized when placed in glass tubes in direct sunlight, the extent of reaction being about the same after four days' exposure as after four hours at 100° C. in the dark. If a little of the polymeric form is added, the polymerization proceeds as far in one day as it does in four days with the pure substance. When p-vinylanisole in quartz tubes at 30° C. is alternately irradiated by a quartz mercury lamp and kept dark, polymerization appears not to proceed during the period of raying, but during the following periods of darkness. It is concluded that rays of wave-length longer than 330 $\mu\mu$ cause polymerization while rays of shorter wave-length reverse the reaction."

If we interpret displacement of equilibrium in the broad sense of passing from one stationary state to another, we shall include all photochemical decompositions. It is not desirable to do this at the present time.

Summary

So long as we confine ourselves to reversible equilibrium the theory of the displacement of equilibrium by light is as simple as can be. The conditions must be such that a photochemical change takes place and that the rate of photochemical change shall be greater than the sum of the rates of the reverse reaction in the dark and in the light. Since one can usually increase the rate of the reverse reaction in the dark considerably relatively to the rates of the photochemical reactions by raising the temperature, the amount of the displacement of equilibrium by any given light usually decreases with rising temperature.

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¹ Z. wiss. Phot., 21, 117 (1922); India Rubber World, 71, 280 (1925).

² Ber., 47, 1793 (1914).

³ J. Russ. Phys. Chem. Soc., 44, 204 (1912).

⁴ Ber., 57B, 484 (1924); Chem. Abs., 18, 2503 (1924).

RELATION BETWEEN PHOTO-CHEMICAL AND IONIZATION REACTIONS

BY S. C. LIND

Both of these classes of reactions may be profitably considered from the standpoint of their quantum relations, the former through the Einstein Equivalence Law, the latter through the principle of ionic-chemical equivalence. The primary step of activation may be regarded in each case as involving a single electron in a single molecule. While the activity of an ion is due to the complete removal of an electron from the molecule acted on, photochemical activation is attributed to the shift of an electron from the normal orbit to one of higher energy, or to a kind of internal ionisation. The energy necessary to ionize is greater than that to excite, accordingly the latent energy possessed by an ion is greater than that of the excited molecule, and one should expect the activity of ions to be more universal and possibly to extend to reactions requiring more energy. Nevertheless the energy of excitation is quite sufficient to accomplish many vigorous and also quite unusual reactions.

Qualitatively one does find some differences of the character just indicated, though perhaps to a less degree than might be expected. Quantitatively, the question presents itself in the form of comparing the yields per quantum and per ion.

As is well known, the yield per light quantum often exceeds the direct prediction of Einstein's law by very large amounts.¹ It has long been stressed by Bodenstein, Stark, Warburg and others that this does not constitute a ground for the rejection of the the Einstein law but is merely an indication that the law holds for the primary step which may be and often is then followed by a chain or cyclical reaction series which may multiply the quantum yield by a large number of cycles. Until recently this assumption had not been tested experimentally, as there was no independent means of determining the primary action or number of cycles.

Using two different activating agencies for the $H_2 + Cl_2$ reaction, light for the production of quanta and α radiation for the generation of ions, Porter, Bardwell and Lind² recently showed that the quantity of HCl formed varies through a wide range of sensitivities of reaction mixture but always in exactly the same degree for the two forms of radiation, hence the length of reaction chains seems to be identical for both. In absolute terms it was found that each chlorine ion (positive or negative) produced about *twice* as many HCl molecules as one light quantum³ (blue). This result shows that, tracing back

¹ A. J. Allmand: Trans. Faraday Soc., 21, 446 (1926).

² J. Am. Chem. Soc., 48, 2603 (1926).

³ There was even some indication that this difference at 25° might disappear at 100°, though this requires further substantiation.

to the primary unit from two independent directions, its reality is established in terms of reaction yield, thus answering one of the most persistent criticisms of the Einstein Law.

Unfortunately there is not a large number of reactions that have been examined for both photo- and ionic activation in the same systems and none, perhaps, where the identity of conditions was insured to the same degree as in $H_2 - Cl_2$ reaction.

One is therefore not justified in concluding that the parallelism holds for all or even a large number of reactions. This reaction ($H_2 + Cl_2$) is the only one known where anything approaching so large a yield per ion ($+ M_{HCl}/N = 5 \times 10^5$) has been found. The next largest, that of polymerization of acetylene ($-M_{C_2H_2}/N = 20$) is much smaller and has none of the characteristics of a chain mechanism, since it remains constant under all circumstances even in the presence of inhibitive oxygen¹ and also of positive catalytic gases.² Unlike the ion yield, departure of quantum yield ($M/h\nu$) from the Einstein equivalence seem to be the rule rather than the exception.

Taylor³ has suggested that the long chain mechanism of photo-reactions is due to the potency not only of free atoms but of free radicals (like C_2H_5 — and CHO —) in maintaining reaction chains. The reactions which Marshall⁴ has examined, however, thought to be long-chained, have proved to be rather short with a yield of the same general order as the M/N yield of the ionic reactions; for example:

for $H_2 + CO$: $-M_{(H_2 + CO)}/h\nu = 4.8$; $-M_{(H_2 + CO)}/N = 3.2$.⁵
 For $H_2 + O_2$: $+M_{H_2O_2}/h\nu = 6.6$;⁶ $+M_{H_2O}/N = 4$; for $2HBr = H_2 + Br_2$ ⁶
 $-M_{HBr}/h\nu = 2$; $-M_{HBr}/N^7 = 2.6$; for NH_3 decomposition $-M_{NH_3}/h\nu^8 = 0.25$; $-M_{NH_3}/N^9 = 0.8$.

Other points of similarity exist with respect to the decomposition of NH_3 by light and by α particles—for example, a positive temperature coefficient due to an increase of quantum yield¹⁰: $-M_{NH_3}/h\nu = 0.4$ at 20° , but 3.3 at 500° ; while $-M_{NH_3}/N = 0.8$ at 18° but 2.5 at 355° .¹¹

It is not only the energy relations which strike one in the photo—and radio-chemical actions but—the fact that reactions ordinarily requiring high temperatures are brought about readily at room temperature. This is no longer surprising when the energy expense per unit of action is considered.

¹ Mund and Koch: *J. Phys. Chem.*, **30**, 289 (1926).

² Lind and Bardwell: *J. Am. Chem. Soc.*, **48**, 1575 (1926).

³ H. S. Taylor: *Trans. Faraday Soc.*, **21**, 560 (1926).

⁴ A. L. Marshall: *J. Phys. Chem.*, **30**, 1078, 1634 (1926).

⁵ Lind and Bardwell: *J. Am. Chem. Soc.*, **47**, 2688 (1925).

⁶ A. L. Marshall: *loc. cit.*

⁷ E. Warburg: *Sitzungsber. Berlin Akad.*, **13**, 314 (1916).

⁸ Lind: *Le Radium*, **8**, 289 (1911).

⁹ E. Warburg: *Sitzungsber. Berlin Akad.*, 1911, 746; 1912, 216.

¹⁰ E. Wourtsel: *Le Radium*, **11**, 289, 332 (1919).

¹¹ K. Kuhn: *Compt. rend.*, **117**, 956; **178**, 708 (1924).

But the directness is surprising with which certain final products are obtained which would usually be possible only through several successive steps; for example, the direct addition¹ of $H_2 + O_2$ to form H_2O_2 or the splitting out of H_2 from two hydrocarbons under ionizing influence to give the hydrocarbon with double the number of C atoms as: $2C_2H_6 = C_4H_{10} + H_2$ ².

In this same connection it is interesting that while ammonia shows no such tendency as do the hydrocarbons to double up with elimination of hydrogen under ionizing influence, Taylor³ has found evidence of the formation of hydrazine when ammonia is acted on by resonated Hg atoms.

On the whole there are some great similarities, but no less striking differences between the photo- and ion reaction mechanisms. In ionisation, clustering seems to be the first step. Theoretically this would be expected from the strong electrostatic attraction exerted by the free charge. It may be this force which prevents disruption and shattering of the molecule under ionizing forces, which is assumed to occur under collisions with photo-sensitized mercury atoms.⁴ Clustering thus prevents chain mechanism and by the same argument we conclude that the chain mechanism does not begin in the $H_2 + Cl_2^+$ (or Cl_2^-) reaction until electrical neutrality has been re-established.⁵

A new and striking case in point may be gained by comparing the recent results of McDonald⁶ on the decomposition of N_2O by ultraviolet light ($\lambda 1860$ to 1990 \AA.U.) with the earlier ones of Wourtsel under α radiation. McDonald finds the quantum yield $-M_{N_2O}/h\nu = 3.9$, while Wurtzel⁷ found $-M_{N_2O}/N = 1.74$ to 2.55 . If we use the Mund Equation⁸ for calculating ionization (N), we are probably justified in multiplying Wourtsel's yield by 1.55 , which brings it into close agreement with McDonald's quantum yield. The fact that both are in accord with the stoichiometric formula $4 N_2O = 3 N_2 + 2 NO_2$ (or $2 NO + O_2$) must suggest "stoichiometric" clustering⁹ about an ionized N_2O molecule on the one hand and an excited one on the other, which is a much more direct mechanism than the steps that have been proposed. Of course at ordinary pressure the excited molecule will exist long enough for the successive clustering collisions to occur. It is to be emphasized that a quadruple collision is not necessary.

From this review, it appears that there is great need for the examination of more reactions by both methods of activation, ionization and excitation, under identical conditions before it can be stated how far the parallel between $M/h\nu$ and M/N yields will extend.

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¹ E. Wourtsel: *Le Radium*, 11, 342 (1919).

² H. S. Taylor: loc. cit.

³ Lind and Bardwell: *J. Am. Chem. Soc.*, 48, 2335 (1926).

⁴ Taylor and Bates: *Proc. Nat. Acad. Sci.*, 12, 714 (1926).

⁵ H. S. Taylor: loc. cit.

⁶ McDonald: *J. Chem. Soc.*, 1928, 1.

⁷ Wourtsel: *Le Radium*, 11, 289 (1919).

⁸ *J. Phys. Chem.*, 30, 894 (Footnote) (1926).

⁹ See Lind: "Chemical Effect of Alpha Particles," 2nd Ed., §68, p. 144 (1928).

LATENT HEAT OF VAPORISATION AS A FUNCTION OF TEMPERATURE

BY RAMSEY M. WINTER

It has been shown by Sugden¹ that for a number of non-associated liquids the classical van der Waals expression for the variation of surface tension with temperature may be written,

$$(1) \quad \gamma = \gamma_0 (1 - T_r)^{6/5}$$

where γ is the surface tension, γ_0 an empirical constant not explicitly derived from the critical data as in the original expression, and T_r the reduced temperature. It has also been demonstrated by Sugden² that for a large number of liquids the difference in density between the liquid and its saturated vapour may be predicted with a high degree of accuracy and over a wide range of temperature by an equation of similar form, namely,

$$(2) \quad D - d = D_0 (1 - T_r)^{3/10}$$

where D and d are the densities of the liquid and vapour respectively. The fact that these two physical properties are thus predictable in terms of only two specific constants one of which is the critical temperature, led the writer to examine the variation with temperature of the latent heat of vaporisation. It was found that this too can be expressed by an equation of the same type,

$$(3) \quad \lambda = \lambda_0 (1 - T_r)^{2/5}$$

In this expression λ is the *total* latent heat of vaporisation, (not the internal latent heat as in the well known formula of Mills connecting latent heats and densities), and λ_0 is a constant to be determined. While this relation like equations (1) and (2) must for the present be regarded as purely empirical, it appears to be quite generally true; its value lies in its application to thermodynamic calculation, in the close connection between latent heat and vapour pressure, and in the development of an independent series of atomic and structural constants analogous to the parachor³ thus opening up a fresh line of attack on problems of chemical structure. It is not proposed to discuss these applications here but to reserve them for separate treatment.

For the purpose of verifying equation (3), great use has been made of the data published by Mills in a long series of papers.⁴ The latent heats of vaporisation of thirty-eight⁵ liquids at temperatures ranging from 0°C. up to the critical temperature were calculated by him from Young's vapour pressure and density data by means of the Clapeyron equation,

¹ J. Chem. Soc., 125, 32 (1924).

² J. Chem. Soc., 129, 1780 (1926).

³ Sugden and co-workers: J. Chem. Soc., 125, 1177 (1924); 127, 1525, 1868, 2517; 128, 139 (1925).

⁴ J. Phys. Chem., 6, 209 (1902); 8, 383, 594 (1904); 9, 402 (1905); 10, 1 (1906); 11, 132, 594 (1907); 13, 512 (1909).

⁵ J. Am. Chem. Soc., 31, 1099 (1909).

$$(4) \quad \lambda = T \frac{dp}{dT} (V - v).$$

To facilitate calculation he expressed the vapour pressure data by means of a Biot formula and computed values of the differential coefficient analytically. The fact that any empirical equation is less reliable near the limits of its range, together with the observation by Mills that the variation of vapour pressure in the vicinity of the critical temperature cannot be accurately expressed by means of a formula of the Biot type, led him to conclude that, "The values at 0° and in the immediate neighbourhood of the critical temperature must, therefore, be excluded from consideration because of errors introduced by the calculation." With this limitation he claimed for his calculated latent heats an accuracy of at least two percent, and stated that "usually the error is less than 1 percent."

Expressing equation (3) in the form

$$(5) \quad \lambda^{5/2}_0 = \lambda^{5/2} (1 - T_r) = \lambda_0^{5/2} - \lambda_0^{5/2} T/T_0$$

it is evident that $\lambda^{5/2}$ should be a linear function of the temperature. This has been tested with Mills' data and found to hold, except for those regions where the data themselves are inaccurate. The values of λ_0 and of T_0 for twenty-two liquids have been obtained by plotting $\lambda^{5/2}$ against temperature, and by taking the best straight line through the points. They are set out in Table I, the observed critical temperatures being inserted for comparison.

TABLE I

| | λ_0 (cals/gram.) | t_0° C. (calc.) | t_0° C. (obs.) |
|----------------------|--------------------------|------------------------|-----------------------|
| Ethane | 174.4 | 33.3 | 32.1 |
| n-Pentane | 131.4 | 197.1 | 197.2 |
| Isopentane | 135.4 | 188.6 | 187.8 |
| n-Hexane | 125.4 | 234.6 | 234.8 |
| n-Heptane | 119.9 | 269.7 | 266.9 |
| n-Octane | 114.1 | 298.5 | 296.2 |
| Methyl Formate | 212.0 | 212.6 | 214.0 |
| Methyl Acetate | 150.6 | 233.4 | 233.7 |
| Ethyl Formate | 145.9 | 233.8 | 235.3 |
| Ethyl Acetate | 134.5 | 150.0 | 250.1 |
| Propyl Formate | 132.5 | 265.3 | 264.9 |
| Methyl Propionate | 134.5 | 257.7 | 257.4 |
| Methyl iso-Butyrate | 118.7 | 268.0 | 267.6 |
| Methyl Butyrate | 121.6 | 283.5 | 281.3 |
| Ethyl Propionate | 125.0 | 273.0 | 272.9 |
| Propyl Acetate | 126.1 | 276.2 | 276.2 |
| Ethyl Ether | 130.4 | 193.6 | 193.6 |
| Carbon Tetrachloride | 82.31 | 286.9 | 283.1 |
| Stannic Chloride | 47.35 | 315.4 | 318.7 |
| Methyl Alcohol | 414.9 | 240.0 | 240.0 |
| Ethyl Alcohol | 330.2 | 238.8 | 243.1 |
| Mercury | 14.71 | 2119 | |

¹ J. Am. Chem. Soc., 31, 1103 (1909).

The results for ethane are obtained from the observations of Parker,¹ while those for mercury are based on the vapour pressure measurements of Smith and Menzies.² In the latter case since the vapour densities at higher temperatures are unknown, the "observed" latent heats had to be calculated by means of the approximate form of the Clapeyron equation,

$$(6) \quad \lambda = RT^2 \frac{d \log p}{dT}$$

As this is accurate only when the specific volume of the liquid is negligible beside that of the vapour, the applicability of equation (3) to mercury could not be tested above 650°K.

The accuracy with which the experimental data can be reproduced from the smoothed values of the constants by means of equation (3) has been tested and the results given in Table II. It will be seen that for the range over which the "observed" data are reliable the agreement is good, the great-

TABLE II

| Ethane | | | | Isopentane | | | |
|--------|------------------|-------------------|-------|------------|------------------|-------------------|-------|
| T°K. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. | t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. |
| 226.2 | 99.95 | 102.0 | +2.05 | 0 | 88.86 | 87.50 | -1.36 |
| 234.6 | 96.70 | 97.70 | +1.00 | 20 | 83.41 | 83.68 | +0.27 |
| 238.9 | 94.79 | 95.25 | +0.46 | 40 | 79.12 | 79.54 | +0.42 |
| 243.2 | 92.76 | 92.89 | +0.13 | 60 | 74.35 | 75.08 | +0.73 |
| 248.6 | 89.56 | 89.50 | -0.06 | 80 | 69.80 | 70.17 | +0.37 |
| 253.0 | 87.30 | 86.70 | +0.40 | 100 | 64.83 | 64.69 | -0.14 |
| 258.8 | 82.13 | 82.81 | +0.68 | 120 | 58.62 | 58.38 | -0.24 |
| 263.3 | 79.84 | 79.58 | -0.26 | 140 | 51.07 | 50.87 | -0.20 |
| 268.7 | 75.75 | 75.44 | -0.31 | 160 | 41.27 | 41.14 | -0.13 |
| 273.1 | 72.06 | 71.79 | -0.27 | 180 | 24.65 | 25.43 | +0.78 |
| 278.8 | 67.16 | 66.59 | -0.55 | 185 | 16.47 | 17.94 | +1.47 |
| 283.6 | 62.88 | 61.69 | -1.19 | | | | |
| 288.3 | 57.85 | 56.25 | -1.60 | | | | |

| n-Pentane | | | | n-Hexane | | | |
|-----------|------------------|-------------------|-------|----------|------------------|-------------------|-------|
| t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. | t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. |
| 0 | 93.36 | 92.81 | -0.55 | 0 | 90.98 | 91.43 | -0.45 |
| 40 | 84.31 | 84.76 | +0.45 | 60 | 80.82 | 81.25 | +0.43 |
| 60 | 80.07 | 80.28 | +0.21 | 80 | 77.55 | 77.45 | -0.10 |
| 80 | 75.33 | 75.37 | +0.04 | 100 | 73.48 | 73.23 | -0.25 |
| 100 | 69.94 | 69.93 | -0.01 | 120 | 69.29 | 68.68 | -0.61 |
| 120 | 64.48 | 63.77 | -0.71 | 140 | 63.84 | 63.59 | -0.25 |
| 140 | 56.58 | 56.54 | -0.04 | 160 | 57.63 | 57.82 | +0.19 |
| 160 | 47.42 | 47.60 | +0.18 | 180 | 50.93 | 51.05 | +0.12 |
| 180 | 35.01 | 34.92 | -0.09 | 200 | 42.75 | 42.54 | -0.21 |
| 195 | 15.66 | 15.15 | -0.51 | 220 | 30.37 | 30.14 | -0.23 |
| | | | | 230 | 19.73 | 19.00 | -0.73 |

¹ J. Am. Chem. Soc., 48, 2058 (1926).

² J. Am. Chem. Soc., 32, 1444 (1910).

TABLE II (Continued)

| n-Heptane | | | | n-Octane | | | |
|-----------|------------------|-------------------|-------|----------|------------------|-------------------|-------|
| t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. | t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. |
| 0 | 89.86 | 90.74 | +0.88 | 0 | 89.46 | 87.98 | -1.48 |
| 80 | 79.44 | 78.81 | -0.63 | 120 | 71.43 | 71.63 | +0.20 |
| 100 | 75.80 | 75.39 | -0.41 | 140 | 68.28 | 68.31 | +0.03 |
| 120 | 71.69 | 71.69 | 0.00 | 160 | 64.75 | 64.71 | -0.04 |
| 140 | 67.12 | 67.70 | +0.58 | 180 | 60.91 | 60.81 | -0.10 |
| 160 | 62.65 | 63.30 | +0.65 | 200 | 56.61 | 56.49 | -0.12 |
| 180 | 58.52 | 58.41 | -0.11 | 220 | 52.03 | 51.57 | -0.46 |
| 200 | 53.17 | 52.81 | -0.36 | 240 | 45.97 | 45.84 | -0.13 |
| 220 | 46.46 | 46.13 | -0.33 | 260 | 39.14 | 38.79 | -0.35 |
| 240 | 37.45 | 37.54 | +0.09 | 280 | 28.26 | 28.93 | +0.67 |
| 260 | 21.90 | 23.96 | +2.06 | 290 | 19.10 | 21.19 | +2.09 |

| Methyl Formate | | | | Methyl Acetate | | | |
|----------------|------------------|-------------------|-------|----------------|------------------|-------------------|-------|
| t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. | t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. |
| 0 | 122.2 | 119.9 | -2.3 | 0 | 109.34 | 110.44 | +1.10 |
| 40 | 111.2 | 110.4 | -0.8 | 60 | 98.59 | 98.06 | -0.53 |
| 60 | 105.1 | 105.1 | 0.0 | 80 | 94.07 | 93.37 | -0.70 |
| 80 | 98.81 | 99.33 | +0.52 | 100 | 88.39 | 88.28 | -0.11 |
| 100 | 92.30 | 93.05 | +0.75 | 120 | 82.87 | 82.73 | -0.14 |
| 120 | 86.22 | 86.04 | -0.18 | 140 | 86.83 | 76.56 | -0.27 |
| 140 | 77.97 | 78.05 | +0.08 | 160 | 69.96 | 69.52 | -0.34 |
| 160 | 68.36 | 68.60 | +0.24 | 180 | 61.00 | 61.20 | +0.20 |
| 180 | 56.48 | 56.65 | +0.17 | 200 | 50.56 | 50.74 | +0.18 |
| 200 | 38.80 | 38.70 | -0.10 | 220 | 34.87 | 35.20 | +0.33 |
| 210 | 22.98 | 20.48 | -2.50 | 230 | 20.99 | 20.30 | -0.69 |

| Ethyl Formate | | | | Ethyl Acetate | | | |
|---------------|------------------|-------------------|-------|---------------|------------------|-------------------|-------|
| t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. | t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. |
| 0 | 106.83 | 107.06 | +0.23 | 0 | 100.6 | 100.1 | -0.5 |
| 60 | 95.82 | 95.08 | -0.74 | 80 | 85.78 | 85.78 | 0.00 |
| 80 | 90.91 | 90.55 | -0.36 | 100 | 82.15 | 81.60 | -0.55 |
| 100 | 85.74 | 85.65 | -0.09 | 120 | 77.53 | 77.05 | -0.48 |
| 120 | 80.26 | 80.28 | +0.02 | 140 | 72.24 | 72.07 | -0.17 |
| 140 | 74.18 | 74.30 | +0.12 | 160 | 65.91 | 66.53 | +0.62 |
| 160 | 67.21 | 67.51 | +0.30 | 180 | 59.87 | 60.16 | +0.29 |
| 180 | 59.44 | 59.48 | +0.04 | 200 | 52.71 | 52.58 | -0.13 |
| 200 | 49.28 | 49.76 | +0.48 | 220 | 42.63 | 42.86 | +0.23 |
| 220 | 34.47 | 34.52 | +0.05 | 240 | 27.17 | 27.62 | +0.45 |
| 230 | 22.79 | 20.61 | -2.18 | 247 | 17.12 | 17.06 | -0.06 |

TABLE II (Continued)

| Propyl Formate | | | | Methyl Propionate | | | |
|----------------|------------------|-------------------|-------|-------------------|------------------|-------------------|-------|
| t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. | t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. |
| 0 | 99.63 | 99.79 | +0.16 | 0 | 100.87 | 100.73 | -0.14 |
| 80 | 87.49 | 86.46 | -1.03 | 80 | 87.07 | 86.80 | -0.27 |
| 100 | 82.66 | 82.58 | -0.08 | 100 | 82.75 | 82.75 | 0.00 |
| 120 | 78.14 | 78.43 | +0.29 | 120 | 78.27 | 78.38 | +0.11 |
| 140 | 73.74 | 73.92 | +0.18 | 140 | 73.42 | 73.62 | +0.20 |
| 160 | 68.29 | 68.96 | +0.67 | 160 | 68.15 | 68.32 | +0.17 |
| 180 | 62.80 | 63.29 | +0.59 | 180 | 62.05 | 62.34 | +0.29 |
| 200 | 56.91 | 56.96 | +0.05 | 200 | 55.67 | 55.37 | -0.30 |
| 220 | 49.62 | 49.20 | -0.42 | 220 | 47.14 | 46.70 | -0.44 |
| 240 | 39.45 | 38.95 | -0.50 | 240 | 34.41 | 34.51 | +0.10 |
| 250 | 31.99 | 31.85 | -0.14 | 250 | 24.30 | 24.76 | +0.46 |
| 260 | 21.02 | 20.81 | +0.79 | 256 | 12.70 | 13.58 | +0.88 |

| Methyl iso-Butyrate | | | | Methyl n-Butyrate | | | |
|---------------------|------------------|-------------------|-------|-------------------|------------------|-------------------|-------|
| t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. | t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. |
| 0 | 91.16 | 89.69 | -1.47 | 0 | 95.79 | 92.83 | -2.96 |
| 100 | 74.77 | 74.40 | -0.37 | 100 | 77.80 | 78.00 | +0.20 |
| 120 | 70.65 | 70.71 | +0.06 | 120 | 74.31 | 74.47 | +0.16 |
| 140 | 66.82 | 66.74 | -0.08 | 140 | 70.84 | 70.69 | -0.15 |
| 160 | 62.12 | 62.34 | +0.22 | 160 | 66.53 | 66.58 | +0.05 |
| 180 | 57.19 | 57.44 | +0.25 | 180 | 62.00 | 62.03 | +0.03 |
| 200 | 52.03 | 51.82 | -0.21 | 200 | 57.41 | 56.93 | -0.48 |
| 220 | 45.16 | 45.08 | -0.08 | 220 | 51.31 | 51.02 | -0.29 |
| 240 | 36.06 | 36.34 | +0.28 | 240 | 44.14 | 43.85 | -0.29 |
| 260 | 21.91 | 22.04 | +0.13 | 260 | 34.44 | 34.29 | -0.15 |
| 265 | 14.53 | 14.90 | +0.37 | 270 | 26.96 | 27.47 | +0.51 |

| Ethyl Propionate | | | | Propyl Acetate | | | |
|------------------|------------------|-------------------|-------|----------------|------------------|-------------------|-------|
| t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. | t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. |
| 0 | 95.00 | 94.71 | -0.29 | 0 | 96.03 | 95.76 | -0.27 |
| 100 | 79.23 | 78.91 | -0.32 | 100 | 79.80 | 79.98 | +0.18 |
| 120 | 75.17 | 75.11 | -0.06 | 120 | 76.33 | 76.25 | -0.08 |
| 140 | 70.19 | 71.03 | +0.84 | 140 | 71.84 | 72.16 | +0.32 |
| 160 | 65.16 | 66.53 | +1.37 | 160 | 67.66 | 67.72 | +0.06 |
| 180 | 59.94 | 61.53 | +1.59 | 180 | 62.80 | 62.79 | -0.01 |
| 200 | 54.66 | 55.85 | +1.19 | 200 | 57.23 | 57.20 | -0.03 |
| 220 | 48.54 | 49.11 | +0.57 | 220 | 50.78 | 50.64 | -0.14 |
| 240 | 40.23 | 40.60 | +0.37 | 240 | 42.40 | 42.46 | +0.06 |
| 260 | 27.84 | 27.87 | +0.03 | 260 | 30.70 | 30.77 | +0.07 |
| 265 | 23.15 | 23.09 | -0.06 | 270 | 20.57 | 20.93 | +0.36 |
| 270 | 15.65 | 15.59 | -0.06 | | | | |

Table II (Continued)

| Ethyl Ether | | | | Carbon Tetrachloride | | | |
|-------------|------------------|-------------------|-------|----------------------|------------------|-------------------|-------|
| t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. | t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. |
| 0 | 92.52 | 91.87 | -0.75 | 0 | 51.87 | 52.38 | +0.51 |
| 20 | 87.54 | 87.82 | +0.38 | 80 | 46.00 | 45.96 | -0.04 |
| 40 | 82.83 | 83.64 | +0.81 | 100 | 44.15 | 44.16 | +0.01 |
| 60 | 78.44 | 79.11 | +0.67 | 120 | 42.08 | 42.19 | +0.11 |
| 80 | 73.50 | 74.13 | +0.63 | 140 | 39.92 | 40.07 | +0.15 |
| 100 | 68.42 | 68.60 | +0.18 | 160 | 37.95 | 37.80 | -0.15 |
| 120 | 62.24 | 62.32 | +0.08 | 180 | 35.40 | 35.30 | -0.10 |
| 140 | 55.33 | 54.89 | -0.44 | 200 | 32.61 | 32.48 | -0.13 |
| 160 | 46.07 | 45.53 | -0.54 | 220 | 29.45 | 29.26 | -0.19 |
| 180 | 31.87 | 31.71 | -0.16 | 240 | 25.56 | 25.38 | -0.18 |
| 190 | 19.38 | 18.63 | -0.75 | 260 | 20.07 | 20.32 | +0.25 |
| | | | | 280 | 10.43 | 11.75 | +1.32 |

| Stannic Chloride | | | | Methyl Alcohol | | | |
|------------------|------------------|-------------------|-------|----------------|------------------|-------------------|-------|
| t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. | t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. |
| 0 | 35.38 | 36.90 | +1.52 | 0 | 289.17 | 305.9 | +16.7 |
| 100 | 31.76 | 31.67 | -0.09 | 20 | 284.54 | 295.4 | +10.9 |
| 120 | 30.54 | 30.47 | -0.07 | 40 | 277.78 | 284.6 | +6.8 |
| 140 | 29.12 | 29.17 | +0.05 | 60 | 269.41 | 272.9 | +3.5 |
| 160 | 27.69 | 27.80 | +0.11 | 80 | 258.96 | 260.2 | +1.2 |
| 180 | 26.29 | 26.31 | +0.02 | 100 | 246.01 | 246.8 | +0.8 |
| 200 | 24.51 | 24.68 | +0.17 | 120 | 232.00 | 232.0 | 0.0 |
| 220 | 22.82 | 22.87 | +0.05 | 140 | 216.12 | 215.7 | -0.4 |
| 240 | 20.86 | 20.82 | -0.04 | 160 | 198.34 | 197.2 | -1.1 |
| 260 | 18.50 | 18.50 | -0.10 | 180 | 177.16 | 175.8 | -1.3 |
| 280 | 15.60 | 15.38 | -0.22 | 200 | 151.84 | 149.5 | -1.3 |
| | | | | 220 | 112.53 | 113.3 | +0.8 |
| | | | | 230 | 84.47 | 85.86 | +1.4 |
| | | | | 236 | 61.66 | 59.53 | -2.1 |

| Ethyl Alcohol | | | | Mercury | | | |
|---------------|------------------|-------------------|-------|---------|------------------|-------------------|-------|
| t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. | t° C. | $\lambda_{obs.}$ | $\lambda_{calc.}$ | Diff. |
| 0 | 220.9 | 243.4 | +22.5 | 300 | 13.94 | 13.94 | 0.00 |
| 20 | 220.6 | 235.1 | +14.5 | 350 | 13.80 | 13.80 | 0.00 |
| 40 | 218.7 | 226.1 | +7.4 | 400 | 13.66 | 13.67 | +0.01 |
| 60 | 213.4 | 216.8 | +3.4 | 450 | 13.52 | 13.53 | +0.01 |
| 80 | 206.4 | 206.7 | +0.3 | 500 | 13.38 | 13.39 | +0.01 |
| 100 | 197.1 | 195.9 | -1.2 | 550 | 13.24 | 13.24 | 0.00 |
| 120 | 184.2 | 184.1 | -0.1 | 600 | 13.10 | 13.10 | 0.00 |
| 140 | 171.1 | 171.0 | -0.1 | 650 | 12.96 | 12.95 | -0.01 |
| 160 | 156.9 | 156.3 | -0.6 | | | | |
| 180 | 139.2 | 139.0 | -0.2 | | | | |
| 200 | 116.6 | 117.7 | +1.1 | | | | |
| 220 | 88.2 | 88.1 | -0.1 | | | | |

est conformity being found in the case of propyl acetate stannic chloride and mercury. Except at the ends of the temperature range the latent heats computed by equation (3) rarely differ by more than half a calorie per gram from the "observed" values, and the differences are usually erratic in sign.

It is of interest to note that the relation (3) holds approximately at higher temperatures even for associated liquids such as methyl and ethyl alcohols. The departure from conformity to the relation with falling temperature probably corresponds to the progressive association of the liquid.

By eliminating the quantity $(1 - T_r)$ between equations (1) (2) and (3) two interesting relations are obtained connecting the latent heat of vaporisation, the liquid and vapour densities, and the surface tension. These relations are,

$$(7) \quad \gamma = \text{const.} \times \lambda^3$$

$$\text{and (8)} \quad \lambda = \text{const.} \times (D - d)^{4/3}.$$

In conclusion I should like to express my thanks to Dr. S. Sugden of Birkbeck College, London, for his lively interest, encouragement, and suggestions in connection with this paper.

*Blackheath,
London, S. E. 3,
December 16, 1927.*

THE SURFACE TENSION AND THE STRUCTURE OF THE SURFACE OF AQUEOUS AMMONIA SOLUTIONS¹

BY OSCAR KNEFLER RICE²

The surface tension of ammonia solutions has previously been measured by Domke,³ Pederson,⁴ and Stocker.⁵ Domke used only three solutions, and his measurements were admittedly inaccurate, being done in open capillaries, so that evaporation could not be controlled. As the other two used the oscillating jet method the interpretation of their results is not unambiguous.⁶

The surface tension of aqueous ammonia solutions has therefore been redetermined, and an attempt has been made to interpret the results.

Experimental Methods and Results

In making measurements on ammonia solutions not only does one have to guard against excessive evaporation, but also, and this is apparently more important, against the action of the solution on glass. This latter factor prevents the use of the drop weight method, for in the time required for the formation of a drop the surface tension might be appreciably altered. It also makes inconvenient the use of a cathetometer for the capillary rise method, though the difficulties could probably be overcome. The method actually adopted consisted in the use of a capillary tube of fairly wide bore with a scale behind it. (See Fig. 1). The capillary, C, approximately half a millimeter in diameter was placed at such an angle as to secure an increase in sensitiveness of about five fold. Directly under it at nearly the same angle,

was the tube B, which was .464 cm. in diameter. These were connected, as shown in Fig. 1, to a wide tube, A, about 2.5 cm. in diameter, and so fixed that they were absolutely rigid. Scales placed back of B and C enabled one to read the position of the meniscus in each of the tubes, first for distilled

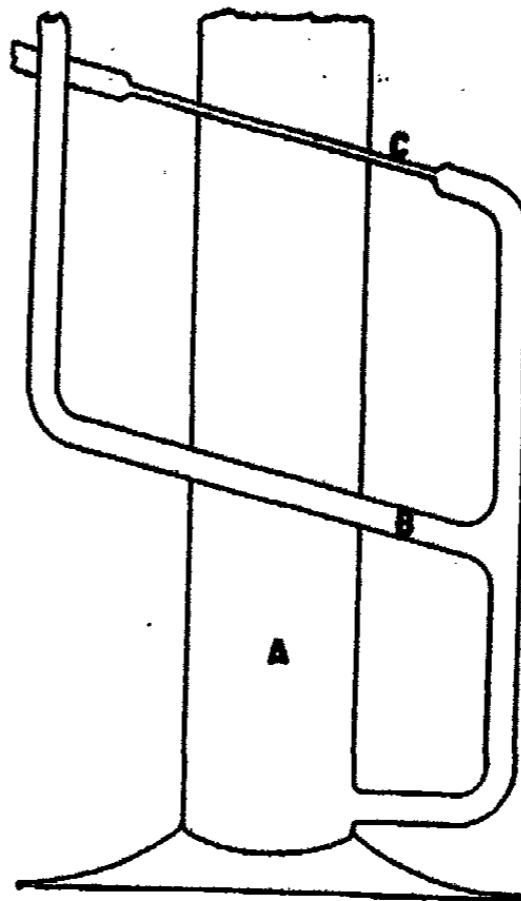


FIG. 1
Diagrammatic Sketch of Apparatus

¹ Contribution from the Chemical Laboratory of the University of California.

² National Research Fellow.

³ Domke: *Wiss. Abh. kaiserlichen Normal-Aichungskomm.*, 3, 65 (1902).

⁴ Pederson: *Phil. Trans.*, 207A, 341 (1908).

⁵ Stocker: *Z. physik. Chem.*, 94, 166 (1920).

⁶ See Rice: *J. Phys. Chem.*, 31, 208 (1927).

water, then for ammonia solution. From the calibration to be described below, the difference in vertical height of the capillary columns of water and ammonia could then be calculated. The height of the capillary column in the case of water (i.e. the difference of capillary rise in C and B) was determined in a way which will also be described later. Knowing the surface tension of water and the density of the solution it is then possible to calculate the difference in surface tension of water and the given solution of ammonia.

The upper end of the tube B communicated with the reservoir tube, A, to insure equalization of pressure. Also, when in use, the upper part of C was connected by means of a piece of rubber tubing to a side arm on the upper part of A, while A itself was closed with a rubber stopper. Thus evaporation was completely prevented. The rubber tube at the upper part of C was also used to manipulate the liquid in the capillary. When a reading was to be made fresh solution was drawn into the capillary from the wide portion of the tube C, the meniscus was brought up above its position of equilibrium and allowed to fall to rest. In the case of the ammonia solutions the meniscus would begin to climb after about half a minute to a minute, indicating an increase of surface tension, probably due to action on the glass, since long standing to insure equilibrium did not seem to prevent it from occurring. In the case of water irregular movements of the meniscus and slight decreases in surface tension sometimes occurred after varying times. However, the first position of the meniscus seemed to be perfectly reproducible, except occasionally when the meniscus behaved erratically.¹

The tubes (mentioned before but not shown in the figure) at the upper part of the apparatus were arranged to support a couple of spirit levels, which were rigidly sealed to the apparatus, and by means of which the apparatus could always be placed in the proper position.

The whole was placed in a water bath, the temperature of which was read, and taken to be the temperature of the substance measured. The effect of temperature on the readings with water and concentrated ammonia solutions was tested, and it was found that the correction was within the limits of error the same for both. A thermostat was not used, but correction made for the temperature.

The apparatus was frequently cleaned during the course of the experiments with concentrated nitric acid.

Calibration of the apparatus and accuracy of the results.

I. Calibration of the scale on B in terms of vertical height.—Mercury was placed in the lower part of A to cut off B and C, and the height in A of a known volume of water from a pipette was measured by a cathetometer, allowance being made for slight movement of the mercury. Then the mercury was removed and liquid from a pipette allowed to drain in, the difference of readings in B being noted. The cross section of B was known, and after allowance was made for the amount of water which entered B itself the change in vertical height for a given difference of readings in B could be determined. This was done for various parts of the scale. I estimate that there may have been introduced in this way a systematic error of $\frac{1}{2}$ to $\frac{3}{4}$ per cent, and an error of perhaps the same amount which would differ in magnitude and sign for different parts of the scale.

¹The length of time the solution stood in the apparatus did not seem to influence the results, and solution in A, obtained by tilting the apparatus, had, within experimental error, the same surface tension as that which had been standing in the narrower tube, except on one occasion when the difference was barely outside the usual experimental error.

II. Measurement of the difference of capillary rise in tubes C and B.—First the vertical height of the estimated center of the meniscus in C above the lowest part of the meniscus in A was measured. To this was added .01 cm. to correct for the difference in level A and a tube of very large diameter.¹ The diameter of B being known the calculated capillary rise was subtracted from the above results. I estimate that these operations were attended with a possible error of $\frac{1}{4}$ to $\frac{3}{4}$ per cent.

The above procedure involves the assumption that the shape of the meniscus for water and an ammonia solution are sufficiently alike in the slanting tube B so as not to cause any appreciable error. The lowest portion of the meniscus in B is read in each case, and we assume in effect that the capillary correction is the same in each case. We estimate that the entire capillary correction, if added say to one reading and not to the other, would make an error of about .4 dyne. Now the surface tension of the most concentrated ammonia solution measured is about 22 per cent less than that of water and its density is about 10 per cent less. If its density were also 22 per cent less it would have exactly the same capillary correction as water. In the actual situation it is obvious that the difference in capillary correction will be a very small fraction of .4 dyne.

III. Readings with water in the apparatus.—From time to time during the course of the experiments, for purposes of calibration, and to check up on the alignment of the apparatus when the scales had to be removed and replaced, many readings were made of the simultaneous levels in B and C of pure water. A reading would be taken, some water removed by a dropper, and another reading taken, and so on, down the length of the scales. In this way a plot of the scale readings against the upper scale reading was made, and the best curve drawn through the points. Some readings were also taken by the method used in the case of the ammonia solutions, several readings being taken without changing the amount of water in the apparatus. It is thought that the curve is correct at all points to within .03 or .04 dyne.

In reading the scale at B parallax was avoided by use of another scale placed so that the marks were seen partly through B and partly outside it. When they appeared straight there was no parallax. The scale on C, itself, served to avoid parallax there.

In order to test the accuracy of the apparatus a series of readings in different parts of the scale for a solution of sodium chloride (Kahlbaum's "für Analyse") of concentration 5.00 moles per liter of solution was made, the values of $\Delta\gamma$ (which we shall use to designate the difference, taken as positive, between the surface tension of water and a solution) being as follows: 9.38, 9.35, 9.26, 9.24, 9.30, 9.35, 9.38. The average, 9.32 agrees well with Harkins and McLaughlin's value² of 9.37. An error of 1 per cent. in either of the calibrations I or II, or in both together, if they were in such directions as to add, would cause an error of about .04 dyne in the final result.

A similar series of readings for an ammonia solution of concentration 3.86 moles per liter gave the following values: 6.90, 6.80, 6.76, 6.75, 6.84, 6.72, 6.86.

By making the calculations it is seen that calibrations I and II have approximately equal effects on the accuracy of the final result, and that an error in either I or II which will increase $\Delta\gamma$ in the case of sodium chloride will decrease it in the case of ammonia. An error in either has more effect on the final result in the case of ammonia (causes about 1.5 to 2 times the percentage error in $\Delta\gamma$). Also, the effect of an error in calibration will vary, but not much, for different concentrations of ammonia. The difference in the various cases is caused by the way the density enters the calculations.

On the whole it seems safe to conclude that errors in the calibrations will not introduce an error appreciably greater than 1 per cent in the final $\Delta\gamma$ values for ammonia solutions. Results from an earlier piece of apparatus of slightly different design, which was broken so that the calibration could not be rechecked, show a systematic deviation from the values here given, $\Delta\gamma$

¹ Richards and Coombs: J. Am. Chem. Soc., 37, 1663 (1915).

² Harkins and McLaughlin: J. Am. Chem. Soc., 47, 2085 (1925).

being about 2 per cent. larger. $\Delta\gamma$ values for salt solutions measured in this apparatus, however, are smaller than those of Harkins and McLaughlin as follows: 2.90 M., 0.13 dynes; 2.00 M., 0.07 dynes; 1.00 M., 0.06 dynes.

As to non-systematic errors, we may expect occasional but infrequent errors up to about 0.1 dynes, since in general a given solution was measured at only one part of the scale.

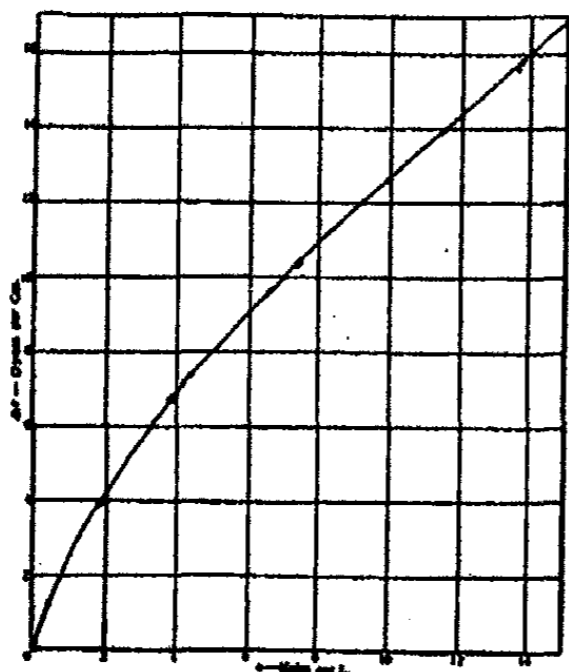


FIG. 2
Difference in Surface Tension of Ammonia
and Water Solutions

Surface tensions were measured on U. S. P. ammonia solutions, and on a C. P. ammonia prepared by passing ammonia gas from a tank into distilled water. This gas was passed through two traps, one containing a small amount of water which quickly became concentrated ammonia solution, and one empty. The latter solution was kept in a Jena glass bottle until diluted just before use, and all measurements on it were made within ten days after it had been prepared.

The concentration of the solutions was determined from the density, ammonia being poured directly from the apparatus into a pycnometer. The table used was that of Runge and Wiernik.¹ The relative density of ammonia solution with respect to water was corrected to 18.5°C., which was close to the temperature at which all the readings were made, and this value used in the calculation of the surface tension.

The final results are given in Table I and plotted in Fig. 2. They do not seem to check the results of previous experimenters.

Adsorption of Ammonia at the Surface

The amount of adsorption is to be calculated from the equation

$$\partial\gamma/\partial n = -\Gamma \partial\bar{F}/\partial n \quad (1)$$

where γ is the surface tension, n the concentration (we shall always use it in moles per liter of solution), \bar{F} the partial free energy of the solute, and Γ is defined by Lewis and Randall² as the amount of solute which must be added to keep the composition of the body of the solution constant when the surface is increased by unity. Since $\bar{F} = RT \log p + \text{const.}$, where p is the partial vapor pressure of ammonia, R the gas constant, and T the absolute temperature³, we may calculate Γ if we know p .

¹ Comey and Hahn: "A Dictionary of Chemical Solubilities," 20 (1921).

² Lewis and Randall: "Thermodynamics," 250 (1923). Γ is called by them n_s .

³ Ammonia vapor is nearly a perfect gas. Landolt-Börnstein: "Tabellen," 269 (1923).

TABLE I
Difference in Surface Tension, $\Delta\gamma$, between Water and Aqueous Solutions of Ammonia at 18.50°C.

| Ammonia | Concentration (Moles per liter of solution) | Density (15/15) | $\Delta\gamma^*$ (Dynes per cm.) |
|---------|---------------------------------------------------|--------------------|-------------------------------------|
| †U.S.P. | .056 | — | .14 |
| †U.S.P. | .45 | .9966 | 1.23 |
| C.P. | 1.83 | .9866 | 3.89 |
| U.S.P. | 1.87 | .9863 | 3.98 |
| C.P. | 3.77 | .9728 | 6.71 |
| U.S.P. | 3.86 | .9721 | 6.80 |
| U.S.P. | 3.92 | .9717 | 6.71 |
| U.S.P. | 4.19 | .9698 | 7.14 |
| C.P. | 4.40 | .9683 | 7.35 |
| C.P. | 6.56 | .9536 | 9.61 |
| U.S.P. | 7.39 | .9481 | 10.39 |
| U.S.P. | 7.39 | .9481 | 10.39 |
| U.S.P. | 7.44 | .9479 | 10.37 |
| U.S.P. | 7.45 | .9478 | 10.39 |
| C.P. | 9.95 | .9315 | 12.63 |
| C.P. | 13.64 | .9083 | 15.60 |
| U.S.P. | 13.81 | .9071 | 15.82 |
| U.S.P. | 14.08 | .9055 | 16.10 |

*The surface tension of ammonia solutions is always less than that of water.
†Measured in different piece of apparatus than that described.

As the figure will be of interest later we have plotted $\log_{10}p$ against n in Fig. 3. The values shown by the plain circles are partial pressures by Perman,¹ while the values designated by circles with a tail are from total pressures by Perman² from which have been subtracted partial pressures of water according to Perman, extrapolated where necessary. The crosses are from Wilson's data³ (Wilson's observed total pressures, corrected for slight differences in temperature, minus Wilson's partial pressure of water interpolated), and the X's are from data of Sims,⁴ corrected by using the now known values of the partial pressure of water. All the data are for 20°C., and it is not worth while to correct to 18.5. The agreement between the various sets of data is very poor, but to get a general idea of the situation we use Perman's as his observations are most numerous. From the slopes in Figs. 2 and 3 we have calculated Γ , which is given for several concentrations in Table II. (For small concentrations a plot of p against n was used instead of Fig. 3).

There are other quantities which are more interesting than the quantity Γ defined as above. Suppose we denote by x the distance from the surface

¹ Perman: J. Chem. Soc., 83, 1168 (1903).

² Perman: J. Chem. Soc., 79, 721 (1901).

³ Wilson: Bull. Eng. Expt. Station, Univ. Illinois, 146, 15, 26 (1925).

⁴ Sims: Ann., 118, 347 (1861).

of the solution¹ and by n_x the concentration of ammonia molecules at a point x . Then we can define a quantity u by the equation

$$u = \int_0^{\infty} u_x dx \quad (2)$$

where $u_x = n_x - n$. Now u will differ² from Γ , for while u is the excess of solute at the surface, and an amount of solute equal to u must be added to the solution to replace it after the surface has been increased by unity, this will not

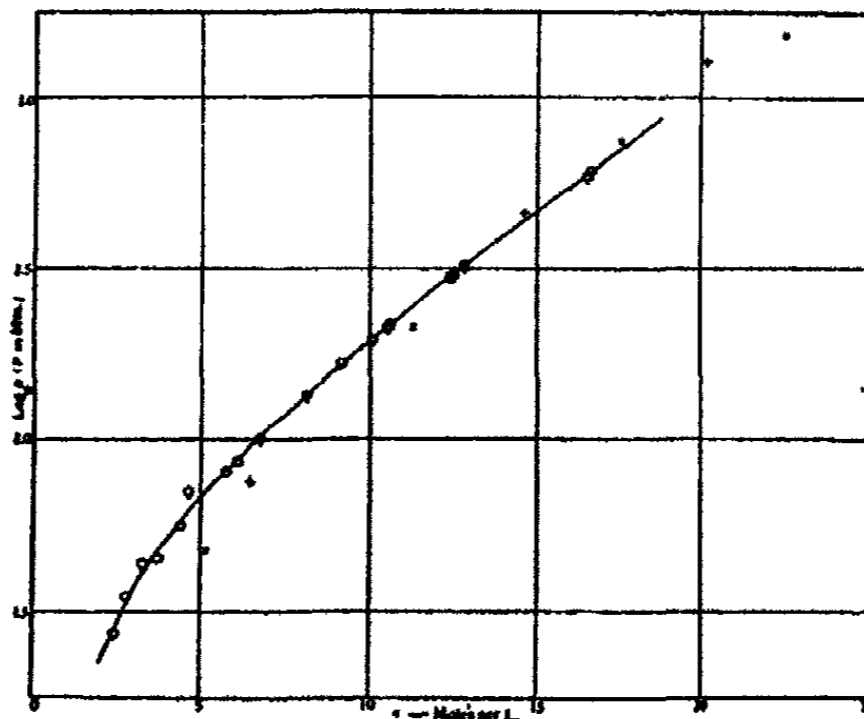


FIG. 3
Vapor Pressure of Ammonia Solutions

be sufficient to bring the concentration of the body of the solution back to its original value, for the molecules of solute adsorbed at the surface have displaced molecules of solvent, and enough solute must be added in addition to u to compensate for this addition of solvent in the body of the solution. If one molecule of solute displaces k molecules of solvent, and if the molal ratio solute to solvent is r , then we will have

$$\Gamma = u(1 + kr) \quad (3)$$

Now from the densities of ammonia solutions it will be found that over a range of concentrations greater than we need to consider, that 1 molecule of ammonia replaces 1.33 molecules of water within about 2 per cent. Thus in a 10 molal solution there are 10 moles of ammonia in a liter, and 42.2 moles of water instead of 55.5 as in pure water. So 10 moles of ammonia replace 13.3 moles of water. It seems, therefore, safe to assume that the adsorption of an ammonia molecule at the surface is attended by practically no change

¹ It is convenient to let $x = 0$ be taken as the position of the center of an ammonia molecule when the molecule is "at the surface." It may be remarked that this method of treatment assumes that the molecules are randomly arranged at the surface, and would be rather ambiguous (though it might be used as an approximation) if there were a fixed film of ammonia molecules at the surface. Later calculations will show that there is probably not such a film.

² Though this is apparently not recognized by Lewis and Randall: *loc. cit.*

in total volume, but that on an average 1.33 molecules of water are forced back into the solution. Thus we may take $k = 1.33$. On this basis we have calculated the values of u given in Table II.

TABLE II
Values of $\Delta\gamma$ and the Adsorption in Ammonia Solutions at 18.50°C.

| n (Moles per l.) | $\Delta\gamma$ (Dynes per cm.) | Adsorption (Moles per sq. cm.) | | |
|-----------------------|-----------------------------------|--------------------------------|--------------------|--------------------|
| | | $\Gamma \times 10^{10}$ | $u \times 10^{10}$ | $U \times 10^{10}$ |
| 1 | 2.40 | .83 | .81 | 1.15 |
| 2 | 4.20 | 1.27 | 1.21 | 1.89 |
| 4 | 6.92 | 1.70 | 1.54 | 2.90 |
| 6 | 9.08 | 1.775 | 1.52 | 3.56 |
| 8 | 10.93 | 1.79 | 1.45 | 4.17 |
| 10 | 12.69 | 1.86 | 1.41 | 4.81 |
| 12 | 14.35 | 1.93 | 1.37 | 5.45 |
| 14 | 16.01 | 1.99 | 1.32 | 6.08 |

Discussion of the Results

If adsorption takes place in a monomolecular layer, as is the usual assumption, in order to get the actual number of moles per unit surface in this layer we should add to u the number of molecules which would be present in a layer of this thickness if no adsorption took place. Taking the thickness of the layer to be 3.4×10^{-8} from the known partial volume of ammonia, we calculate for the total number of moles per unit surface the values given under U in Table II. For the value of U in molecules per sq. cm. we get for a concentration of 14 M, 3.7×10^{14} , which means that the distance between centers of adjacent ammonia molecules is 5.2×10^{-8} cm., which would seem to indicate that the layer is not filled, as is also indicated by the fact that U does not approach a constant value.

In spite of this fact, one infers, from what is known about molecular forces, and from the numerous researches on similar phenomena, that the adsorbed molecules will be very close to the surface. The average distance of the ammonia molecules from the surface could actually be determined if we had measurements of the dynamic surface tension, γ' , which we knew were measurements of a surface formed so rapidly that no adsorption had taken place, but so slowly that equilibrium was established throughout as far as the solvent was concerned. For, as we have shown¹

$$\lim_{n \rightarrow 0} d\gamma'/dn = -RT \int_0^\infty \log(n_x/n) dx = \int_0^\infty W_x dx \quad (4)$$

where W_x is the work due to the forces of adsorption of bringing a mole of solute from the body of the solution to a point x (so that $RT \log(n_x/n) = -W_x$ for dilute solutions).²

¹ Rice: *loc. cit.*, equation (7). (The sign of the integral in parentheses in this equation is incorrect.)

² See Herzfeld: *Z. physik. Chem.*, 107, 74 (1923).

Now suppose we assume, in order to get an idea of the average distance of the adsorbed molecules from the surface of the solution, that if x is less than some distance a then W_x has a constant value W_a , and for $x > a$ that $W_x = 0$. Then for $x < a$ it is seen that n_x has some constant value n_a , and for $x > a$ we have $n_x = n$. We then have $\int_0^{\infty} W_x dx = aW_a$, or

$$d\gamma'/dn = aW_a \quad (5)$$

while Gibbs's equation (1) gives us (since for small concentrations $1 + kr = 1$)

$$\begin{aligned} d\gamma/dn &= -RTu/n = -RT(n_a - n)a/n \\ &= -RTa \left(e^{-W_a/RT} - 1 \right) \end{aligned} \quad (6)$$

which gives two equations¹ for a and W_a .

As it seems likely that it will be some time before we can make an unambiguous interpretation of the so-called dynamic measurements of surface tension, we shall attempt to make an estimate of the quantity $\int_0^{\infty} W_x dx$ from the

data at hand. We are able to do this because the curve of Fig. 3 is nearly a straight line over a large range of concentrations. It unfortunately requires, however, that we make an extrapolation from this range of concentrations to infinite dilution which is not entirely without objections.

The molecules at the surface are acted upon by forces of adsorption, and have an energy due to these forces equal, per mole, as we have seen, to W_x . This will always be balanced by the effect due to the increase of concentration, which we may write in general as $u_x \Delta \bar{F} / \Delta n$, where $\Delta \bar{F} / \Delta n$ is a measure of the increase of partial free energy with concentration. We have.

$$u_x \Delta \bar{F} / \Delta n = -W_x \quad (7)$$

Equation (7) may if desired be considered as definitional of W_x , $\Delta \bar{F} / \Delta n$ being the same for changes in concentration at the surface as in the body of the solution. Now in the region in which $\log p$ or \bar{F} has a straight line relation with n , equation (7) becomes

$$u_x \partial \bar{F} / \partial n = -W_x \quad (8)$$

in which case, since $\partial \bar{F} / \partial n$ does not depend on x ,

$$\int_0^{\infty} u_x (\partial \bar{F} / \partial n) dx = u \partial \bar{F} / \partial n = - \int_0^{\infty} W_x dx \quad (9)$$

Since it is seen by Fig. 3 that we always have $\partial \bar{F} / \partial n \approx \Delta \bar{F} / \Delta n$ we have from (1), (3) and (7)

$$-d\gamma/dn / (1 + kr) \approx - \int_0^{\infty} W_x dx \quad (10)$$

Equality occurs where $\log n$ or \bar{F} against n is a straight line.

¹ In these considerations we have tacitly assumed that only one species of ammonia molecule is present, but the considerations remain unaltered if we neglect association at low concentrations (as seems justified by the partial vapor pressure of water) and assume that equilibrium between various hydrates is unaltered at the surface. We neglect ionization of the ammonia, which is permissible since all the measurements used were made at concentrations where it is negligible.

We have plotted $-\frac{d\gamma}{dn}/(1+kr)$ against n in Fig. 4. It is seen that in the region where it is approximately equal to $-\int_0^\infty W_x dx$ the curve is linear and nearly horizontal. Assuming that this relation holds throughout the range of concentrations we have extrapolated the straight part of the curve to $n=0$, and obtain as the limit 8.8×10^2 erg cm. per mole.

Using this value, and the value of $d\gamma/dn$, which from Fig. 2 is 2.7×10^3 dynes per cm., per mole per cc., we obtain from (4), (5), and (6) the value for a of 1.9×10^{-8} . a is rather sensitive to changes in $\int_0^\infty W_x dx$. Thus if we had

used 10.0×10^2 instead of 8.8×10^2 we would have obtained 2.35×10^{-8} for a . So we cannot fix the value of a with any degree of exactness, but the evidence is in favor of the adsorption taking place close to the surface, i.e. within distances comparable with the size of a molecule, as we should expect. It should be noted that the average distance of the center of an adsorbed molecule from the surface will be $a/2$, or about 10^{-8} cm., according to our estimate.¹

In order to check our work we have calculated u for several concentrations in Table III. To do this we find $W_a a$ from Fig. 3, calculate W_a , use the curve of Fig. 2 to pick out a concentration, n_a , such that the difference in partial free energy for that concentration and for the concentration, n , of the body of the solution just balances W_a , and finally compute u which is equal to $a(n_a - n)$. The check for the values of u merely indicates that the extrapolation for $\int_0^\infty W_x dx$ or $W_a a$ is a possible one, and does not exclude others. The difference for observed and calculated u 's in the case of $n = 10$ is an indication of how far from being correct our assumption is that $\Delta\bar{F}/\Delta n = \partial\bar{F}/\partial n$, and therefore that we can use the equal sign in (10), for large n 's. It would put us in a position to get a second approximation for $\int_0^\infty W_x dx$, but it is not worth while

to do this without better values for the vapor pressures.

It is to be noted that the validity of our estimation of a depends only on the extrapolation for $\int_0^\infty W_x dx$, and on the linearity of the n -log p curve, and not on the actual values of the vapor pressure. From the values of u_x in Table III it will be seen that the linearity must extend about 6 or 7 moles per

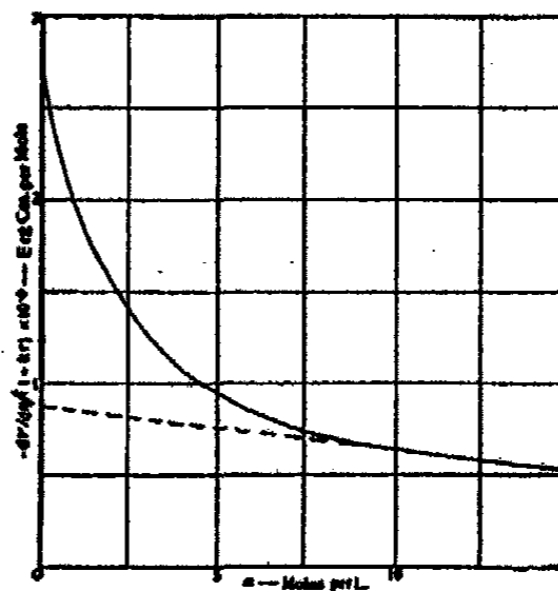


FIG. 4

¹ See reference 1 on p. 588.

TABLE III

Calculation of u from the Extrapolation of Fig. 4 ($a = 1.9 \times 10^{-8}$ cm.)

| n (Moles per l) | $\int_0^\infty W dx \times 10^{-2}$ (Erg cm. per mole) | $W_a \times 10^{-10}$ (Erg per mole) | u_x (Moles per l) | $u \times 10^{10}$ (Moles per sq. cm.) | $u \times 10^{10}$, obs. (Moles per sq. cm.) |
|----------------------|--------------------------------------------------------------|--------------------------------------------|------------------------|----------------------------------------------|-----------------------------------------------------|
| 2 | 8.3 | 4.36 | 6.1 | 1.16 | 1.21 |
| 4 | 7.9 | 4.15 | 8.2 | 1.56 | 1.54 |
| 6 | 7.4 | 3.89 | 8.6 | 1.63 | 1.52 |
| 10 | 6.4 | 3.37 | 8.2 | 1.56 | 1.41 |

liter beyond the highest concentration for which we attempt to find $\int_0^\infty W_x dx$.

It may be verified that the particular set of assumptions we make as to the conditions at the surface will not greatly affect our estimation of the average distance of an adsorbed molecule from the surface, which may be defined as $(1/u) \int_0^\infty x u_x dx$. For example, suppose that for $x > a$ we have $W_x = 0$, while W_x is proportional to $a - x$ when x is less than a . Working this case out, and using the same value for $\int_0^\infty W_x dx$ at $n = 0$ as before, (8.8×10^2) we find for a the value 2.6×10^{-8} . In the region where the n -log p curve is a straight line, and approximately elsewhere, we find in this case that the average distance of an adsorbed molecule is $a/3$. It is seen that the agreement with the previous estimate is very close.

Summary

The surface tension of aqueous ammonia solutions has been measured by a modified capillary rise method over a range of concentrations from 0 to 14 moles per liter.

The adsorption, defined in several different ways, of the ammonia at the surface of the solution has been calculated.

From these calculations it appears that there are not enough ammonia molecules at the surface to fill a monomolecular layer, even at the highest concentrations used.

The work, W_x , done on a mole of ammonia when it is brought from the body of the solution to a distance x from the surface is balanced by the change in partial free energy due to that increased concentration of ammonia at the point x . By a consideration of these relations, using the partial pressure curve for ammonia, it is shown that $\int_0^\infty W_x dx$ is a linear, slightly decreasing (in magnitude, disregarding sign) function of the concentration in the body of the solution, for the higher concentrations used. By extrapolating this linear relationship to infinite dilution, and using the laws of dilute solutions, it is estimated that the average adsorbed molecule is about 10^{-8} cm. from the surface. More definite information could be obtained on this point by the measurement of dynamic surface tensions, if they could be unambiguously interpreted.

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SOLUBILITY RELATIONS OF ISOMERIC ORGANIC COMPOUNDS
VII. The Mutual Solubility of the Dinitrobenzenes with the Nitroanilines,
and of the three Chlorobenzoic Acids*

BY JOHN JOHNSTON AND EDWIN P. JONES¹

In two previous papers it was shown that solutions of the three dinitrobenzenes,² and of the three nitroanilines³ are substantially ideal with respect to the mutual solubility of the several isomers; the present paper extends the measurements to the other nine binary systems—namely of each nitroaniline with each dinitrobenzene—for it was of interest to ascertain if these pairs behave similarly, as in fact they do. The mutual solubility in the three binary systems of the chlorobenzoic acids was also determined; with the results that these systems also prove to be substantially ideal in this respect. On the other hand, the pairs of like isomers of the chloronitrobenzenes and bromonitrobenzenes appear in each of the three cases to form an unbroken series of mix-crystals; *p*-nitrobenzoic acid and *p*-toluic acid show only partial crystal miscibility.

The Dinitrobenzenes with the Nitroanilines

The method of purification and the criterion of purity was the same as previously described.^{2,3} The experimental procedure was somewhat different in that the solid system, contained in a tube surrounded, as before, by a heating coil and a Dewar vessel,⁴ was *slowly* heated, and the temperature at which the last crystal just disappeared was observed directly; during this process the mixture was continuously stirred by the rotation, forward and reverse, of a smaller tube enclosing the thermoelement. This procedure, when carefully carried out, yields a result entirely comparable with that derived from a series of cooling curves, properly interpreted, and is more rapid; it is advantageous particularly for systems in which the stable solid phase crystallizes sluggishly, as proved to be the case with *o*- and *m*-nitroaniline and *m*-dinitrobenzene from some of the mixtures. Each experimental datum in the tables is the average of at least two concordant observations of the last melting temperature *t* (centigrade) of the mixture containing the mol percentage C_A of substance A.

Discussion. In order to secure a better comparative picture of the several solubilities the results were plotted in terms of $\log N$ vs. $1000/T$ on a large scale, and values read off at regular intervals of the reciprocal temperature.

*Contribution from the Department of Chemistry, Yale University.

¹From the dissertation presented by Edwin P. Jones to the Graduate School of Yale University in June 1926, in candidacy for the degree of Doctor of Philosophy.

²Andrews: *J. Phys. Chem.*, 29, 1041 (1925).

³Kohman: *J. Phys. Chem.*, 29, 1048 (1925). Compare also *ibid.*, 29, 882, 914, 1317 (1925); 30, 70 (1926).

⁴Arranged so that the mixture within could be illuminated and observed.

These are presented in Tables III and IV, along with values similarly interpolated from the respective data of Andrews³ and of Kohman,⁴ and the ideal value as derived from the calorimetric data of Andrews, Lynn and Johnston.⁵ As the values finally published differ, owing to the adoption of a better value for the specific heat of the silver standard, from those used in the previous similar calculations, they are tabulated below, together with the coefficients derived from them in the ideal solubility equation⁶

TABLE I

Experimental Data on the Solubility of the Solid Phase A in Mixture with the Second Component B.

(1) A = *o*-Dinitrobenzene

| B = <i>o</i> -Nitroaniline | | <i>m</i> -Nitroaniline | | <i>p</i> -Nitroaniline | |
|----------------------------|-------|------------------------|-------|------------------------|-------|
| C _A | t | C _A | t | C _A | t |
| 100.0 | 116.8 | 100.0 | 116.8 | 100.0 | 116.8 |
| 76.5 | 102.9 | 87.5 | 109.9 | 87.9 | 110.5 |
| 56.0 | 87.5 | 74.9 | 101.8 | 76.6 | 104.4 |
| 36.0 | 68.8 | 60.1 | 90.8 | 70.0 | 99.8 |
| Eutectic | 54.0 | Eutectic | 81.2 | Eutectic | 93.3 |

(2) A = *m*-Dinitrobenzene

| | | | | | |
|----------|------|----------|------|----------|------|
| 100.0 | 89.8 | 100.0 | 89.8 | 100.0 | 89.8 |
| 75.5 | 72.5 | 87.8 | 82.2 | 89.5 | 83.6 |
| 54.6 | 53.0 | 76.9 | 73.7 | 74.8 | 72.5 |
| 46.5 | 43.4 | 66.9 | 64.9 | | |
| Eutectic | 37.8 | Eutectic | 61.0 | Eutectic | 70.1 |

(3) A = *p*-Dinitrobenzene

| | | | | | |
|----------|-------|----------|-------|----------|-------|
| 100.0 | 172.8 | 100.0 | 172.8 | 100.0 | 172.8 |
| 76.0 | 156.7 | 89.0 | 166.6 | 86.5 | 165.2 |
| 55.9 | 138.9 | 78.3 | 159.1 | 69.4 | 154.0 |
| 35.6 | 114.6 | 61.8 | 145.7 | 55.1 | 142.0 |
| 18.2 | 79.0 | 49.3 | 133.1 | 52.5 | 139.0 |
| | | 36.6 | 117.5 | 44.4 | 131.3 |
| | | 27.6 | 102.5 | 37.4 | 122.2 |
| Eutectic | 62.0 | Eutectic | 97.1 | Eutectic | 119.3 |

$$\log N_A = K_1 \left(\frac{T_A - T}{T} \right) + K_2 \log \frac{T_A}{T} + K_3 (T_A - T)$$

T_A denoting the absolute melting temperature of pure A and T the last melting temperature (absolute) of a mixture containing the mole fraction N_A of A (C_A = 100 N_A).

³ J. Am. Chem. Soc., 48, 1274 (1926).

⁶ Cf. Andrews: ref. 2, p. 1043.

TABLE II
Experimental Data on the Solubility of the Solid Phase A in Mixture with
the Second Component B.

| (1) A = <i>o</i> -Nitroaniline | | | | | |
|--------------------------------|-------|--------------------------|-------|--------------------------|-------|
| B = <i>o</i> -Dinitrobenzene | | <i>m</i> -Dinitrobenzene | | <i>p</i> -Dinitrobenzene | |
| C _A | t | C _A | t | C _A | t |
| 100.0 | 69.9 | 100.0 | 69.9 | 100.0 | 69.9 |
| 90.7 | 64.7 | 90.3 | 63.1 | 90.1 | 64.4 |
| 81.6 | 59.3 | 80.8 | 55.9 | | |
| Eutectic | 54.0 | 69.0 | 47.3 | Eutectic | 62.0 |
| | | 61.7 | 41.1 | | |
| | | Eutectic | 37.8 | | |
| (2) A = <i>m</i> -Nitroaniline | | | | | |
| 100.0 | 112.0 | 100.0 | 112.0 | 100.0 | 112.0 |
| 83.5 | 103.8 | 91.4 | 107.7 | 91.2 | 108.0 |
| 74.7 | 98.7 | 89.4 | 106.7 | 80.7 | 101.8 |
| 65.8 | 93.3 | 76.3 | 98.7 | | |
| 64.9 | 93.2 | 74.9 | 97.5 | | |
| 55.6 | 86.3 | 64.7 | 89.7 | | |
| 50.7 | 82.8 | 57.7 | 83.8 | | |
| | | 49.0 | 75.6 | | |
| | | 37.5 | 63.2 | | |
| Eutectic | 81.2 | Eutectic | 61.0 | Eutectic | 97.1 |
| (3) A = <i>p</i> -Nitroaniline | | | | | |
| 100.0 | 147.5 | 100.0 | 147.5 | 100.0 | 147.5 |
| 84.3 | 137.1 | 90.8 | 141.5 | 91.6 | 142.3 |
| 63.9 | 121.6 | 84.3 | 136.8 | 82.6 | 135.4 |
| 54.2 | 112.6 | 73.2 | 127.3 | 70.6 | 125.2 |
| 43.4 | 100.2 | 62.0 | 116.7 | | |
| | | 50.2 | 103.5 | | |
| | | 41.5 | 93.1 | | |
| | | 33.8 | 81.8 | | |
| Eutectic | 93.3 | Eutectic | 70.1 | Eutectic | 119.3 |

| Substance | Heat of melting (cal.) at t | T _A | K ₁ | K ₂ | K ₃ |
|--------------------------|---------------------------------------|----------------|----------------|----------------|----------------|
| <i>o</i> -dinitrobenzene | 4245 + 15.81t - 0.0460 t ² | 389.9 | 1.964 | -20.60 | 0.01005 |
| <i>m</i> - " | 2224 + 26.49t - 0.0565 t ² | 362.9 | 5.556 | -28.86 | 0.01235 |
| <i>p</i> - " | 5893 + 3.41t + 0.0077 t ² | 445.9 | -2.714 | +0.401 | -0.00168 |
| <i>o</i> -nitroaniline | 2773 + 20.2t - 0.0382 t ² | 343.0 | 3.564 | -20.67 | 0.00835 |
| <i>m</i> - " | 4224 + 19.2t - 0.0650 t ² | 385.1 | 3.330 | -27.53 | 0.01421 |
| <i>p</i> - " | 3015 + 23.0t - 0.0630 t ² | 420.6 | 4.139 | -28.89 | 0.01377 |

TABLE III

Comparison of the Solubility (in terms of C_A , mol percentage of solute) of the Dinitrobenzenes in various solvents at even intervals of $1000/T$.

| (a) A = <i>ortho</i> | | | | | | | |
|---------------------------------------|----------|-------|-------|-------|-------|------|------|
| | $1000/T$ | 2.60 | 2.70 | 2.80 | 2.90 | 3.00 | |
| Solvent | t | 111.5 | 97.3 | 84.0 | 71.7 | 60.2 | |
| Ideal | | | | | | | |
| <i>m</i> -dinitrobenzene ² | | 90.7 | 69.2 | 52.9 | 40.8 | 31.6 | |
| <i>p</i> " " | | 90.7 | 70.1 | 55.2 | 44.3 | | |
| <i>o</i> -nitroaniline | | 91.2 | | | | | |
| <i>m</i> - " " | | 90.7 | 68.5 | 51.8 | 39.1 | 29.5 | |
| <i>p</i> - " " | | 90.6 | 68.5 | 52.0 | | | |
| | | 89.8 | 65.9 | | | | |
| (b) A = <i>meta</i> | | | | | | | |
| | $1000/T$ | 2.80 | 2.90 | 3.00 | 3.10 | 3.20 | |
| Solvent | t | 84.0 | 71.7 | 60.2 | 49.5 | 39.4 | |
| Ideal | | | | | | | |
| <i>o</i> -dinitrobenzene ² | | 91.5 | 74.8 | 62.0 | 52.1 | 44.1 | |
| <i>p</i> - " " | | 91.6 | 75.4 | | | | |
| <i>o</i> -nitroaniline | | 91.1 | | | | | |
| <i>m</i> - " " | | 91.5 | 74.6 | 60.8 | 49.6 | 40.4 | |
| <i>p</i> - " " | | 91.4 | 74.5 | | | | |
| | | 91.1 | 73.8 | | | | |
| (c) A = <i>para</i> | | | | | | | |
| | $1000/T$ | 2.30 | 2.40 | 2.50 | 2.60 | 2.70 | 2.80 |
| Solvent | t | 161.7 | 143.6 | 126.9 | 111.5 | 97.3 | 84.0 |
| Ideal | | | | | | | |
| <i>o</i> -dinitrobenzene ² | | 82.5 | 59.2 | 42.7 | 30.9 | 22.5 | 16.4 |
| <i>m</i> - " " | | 80.9 | 57.4 | 41.1 | 29.6 | | |
| <i>o</i> -nitroaniline | | 81.7 | 59.3 | 43.9 | 33.0 | 24.8 | 18.5 |
| <i>m</i> - " " | | 82.9 | 60.8 | 45.0 | 33.6 | 25.7 | 20.1 |
| <i>p</i> - " " | | 81.7 | 59.2 | 44.1 | 33.0 | 24.9 | |
| | | 81.4 | 56.9 | 41.0 | | | |

²D. H. Andrews, loc. cit.

TABLE IV

Comparison of the Solubility (in terms of C_A , mol percentage of solute) of the Nitroanilines in various solvents at even intervals of $1000/T$.

| (a) A = <i>ortho</i> | | | | |
|-------------------------------------|---------------|---------|------|------|
| Solvent | $1000/T$ t | 3.00 | 3.10 | 3.20 |
| | | 60.2 | 49.5 | 39.4 |
| Ideal | | 84.6 | 70.1 | 58.4 |
| <i>m</i> -nitroaniline ³ | | 88.0 | | |
| <i>p</i> - " ³ | | 85.7 | | |
| <i>o</i> -dinitrobenzene | | 83.0 | | |
| <i>m</i> - " | | 86.0 | 72.1 | 60.3 |
| <i>p</i> - " | | [83.3]* | | |

| (b) A = <i>meta</i> | | | | | |
|-------------------------------------|---------------|------|------|------|------|
| Solvent | $1000/T$ t | 2.70 | 2.80 | 2.90 | 3.00 |
| | | 97.3 | 84.0 | 71.7 | 60.2 |
| Ideal | | 75.1 | 57.1 | 43.7 | 33.6 |
| <i>o</i> -nitroaniline ³ | | 73.7 | 55.6 | 42.1 | 32.4 |
| <i>p</i> - " ³ | | 73.7 | | | |
| <i>o</i> -dinitrobenzene | | 72.1 | 52.5 | | |
| <i>m</i> - " | | 74.5 | 58.0 | 45.1 | |
| <i>p</i> - " | | 72.8 | | | |

| (c) A = <i>para</i> | | | | | | | |
|-------------------------------------|---------------|-------|-------|-------|------|------|------|
| Solvent | $1000/T$ t | 2.40 | 2.50 | 2.60 | 2.70 | 2.80 | 2.90 |
| | | 143.6 | 126.9 | 111.5 | 97.3 | 84.0 | 71.7 |
| Ideal | | 94.6 | 73.6 | 57.6 | 45.5 | 36.1 | 28.9 |
| <i>o</i> -nitroaniline ³ | | 94.2 | 72.7 | 57.2 | 45.1 | 35.3 | 27.7 |
| <i>m</i> - " ³ | | 94.7 | 74.0 | 57.8 | 45.7 | | |
| <i>o</i> -dinitrobenzene | | 93.8 | 70.2 | 53.1 | 41.2 | | |
| <i>m</i> - " | | 93.9 | 72.6 | 57.0 | 44.8 | 35.2 | |
| <i>p</i> - " | | 93.9 | 72.5 | | | | |

³ G. T. Kohman, loc. cit.

* Below eutectic temperature.

The data of Tables III and IV show that there is a reasonably close concordance between the several solubility curves for each solid phase in these binary systems. In some cases the concentration for a given temperature is somewhat below, in others it is slightly above, the calculated ideal; and in a few cases the experimental curve appears to cross the ideal. In general, the divergence is greatest when the melting temperatures of the pair of components are farthest apart; but there does not appear to be any specific difference as between systems composed of a pair of dinitrobenzenes or of nitroanilines, on the one hand, and of a dinitrobenzene and a nitroaniline, on the other. It is doubtful in how far this last statement can be generalized; for there will almost certainly prove to be cases in which the solubility of an isomer A, in mixture with isomer B having another pair of substituent groups, is not ideal even though the solubility both of A and B is substantially ideal in binary mixtures of the triads of A and of B respectively.

Another illustrative comparison is between the eutectic temperature as observed, and that derived by extrapolation to intersection of the pair of experimental solubility curves, as listed in Table V. The extrapolated temperature is, on the average, 0.8° higher than the observed which, being independent of the relative amounts of liquid and solid, is more likely to be

TABLE V

The Observed Eutectic Temperature, and the Extrapolated Eutectic Temperature and Composition (in mol percentage to the nearest 0.1%) in the Several Binary Systems of the Dinitrobenzenes (D) and the Nitroanilines (N).

| Components | | Eutectic Temperature | | | Eutectic Composition | |
|-------------|-------------|----------------------|--------------|-------|----------------------|----------------|
| 1 | 2 | Observed | Extrapolated | Diff. | C ₁ | C ₂ |
| <i>o</i> -D | <i>o</i> -N | 54.0 | 54.8 | 0.8 | 25.6 | 74.4 |
| <i>o</i> -D | <i>m</i> -N | 81.2 | 82.1 | 0.9 | 50.0 | 50.0 |
| <i>o</i> -D | <i>p</i> -N | 93.3 | 94.0 | 0.7 | 61.1 | 38.9 |
| <i>m</i> -D | <i>o</i> -N | 37.8 | 39.0 | 1.2 | 40.0 | 60.0 |
| <i>m</i> -D | <i>m</i> -N | 61.0 | 62.4 | 1.3 | 63.1 | 36.9 |
| <i>m</i> -D | <i>p</i> -N | 70.1 | 70.7 | 0.6 | 72.4 | 27.6 |
| <i>p</i> -D | <i>o</i> -N | 62.0 | 62.5 | 0.5 | 13.0 | 87.0 |
| <i>p</i> -D | <i>m</i> -N | 97.1 | 98.4 | 1.3 | 25.4 | 74.6 |
| <i>p</i> -D | <i>p</i> -N | 119.3 | 119.4 | 0.1 | 35.4 | 64.6 |

right. This indicates that the method of experiment—namely to observe the temperature at which the last crystal disappears when the system is slowly heated—tends to yield somewhat too high temperatures for a given gross composition; and this would be expected since the real concentration of the disappearing solid phase in the liquid is somewhat smaller than the gross concentration in the mixture as a whole. This is just the converse of what happens in the more usual method of observing the cooling or freezing curve,

where it is necessary to allow for the amount of solid which has separated out at the moment when the temperature is read; otherwise, the temperature read as corresponding to a given initial composition is too low.⁷

The Chlorobenzoic Acids

To purify each of these substances, it was dissolved in a solution of sodium hydroxide, which was then filtered and acidified; it was recrystallized from water, and then sublimed. The product in each case showed an acceptable cooling curve. The observations on the three binary systems, together with a few made in the ternary mixtures, are listed in Table VI.

TABLE VI
Experimental Data on the Mutual Solubility of the Three Chlorobenzoic Acids

| System <i>o-m</i> | | | System <i>o-p</i> | | | System <i>m-p</i> | | |
|-------------------|----------|-------------|-------------------|----------|-------------|-------------------|----------|-------------|
| Mol % <i>o</i> | <i>t</i> | solid phase | Mol % <i>o</i> | <i>t</i> | solid phase | Mol % <i>m</i> | <i>t</i> | solid phase |
| 100.0 | 139.9 | <i>o</i> | 100.0 | 139.9 | <i>o</i> | 100.0 | 153.5 | <i>m</i> |
| 90.4 | 135.1 | " | 93.3 | 137.0 | " | 90.9 | 149.0 | " |
| 80.1 | 128.5 | " | 88.9 | 134.3 | " | 85.3 | 145.3 | " |
| 71.4 | 122.8 | " | — | 131.8 | <i>o-p</i> | — | 140.0 | <i>m-p</i> |
| 70.7 | 122.2 | " | 84.8 | 134.9 | <i>p</i> | 77.3 | 145.4 | <i>p</i> |
| 58.3 | 112.6 | " | 77.5 | 153.0 | " | 62.9 | 176.0 | " |
| — | 108.7 | <i>o-m</i> | 74.3 | 160.3 | " | 49.2 | 196.2 | " |
| 52.1 | 111.3 | <i>m</i> | 70.1 | 170.1 | " | 45.9 | 200.2 | " |
| 50.1 | 114.3 | " | 59.3 | 186.9 | " | 35.0 | 212.7 | " |
| 40.8 | 123.8 | " | 39.4 | 209.4 | " | 23.8 | 222.7 | " |
| 30.9 | 132.6 | " | 26.9 | 220.9 | " | 9.6 | 233.3 | " |
| 23.5 | 138.7 | " | 22.6 | 223.6 | " | 0.0 | 239.5 | " |
| 15.7 | 144.3 | " | 9.6 | 233.5 | " | | | |
| 9.8 | 148.2 | " | 0.0 | 239.5 | | | | |
| 0.0 | 153.5 | " | | | | | | |

Ternary System *o-m-p*

| Mol % | <i>o</i> | <i>m</i> | <i>p</i> | <i>t</i> | solid phase |
|-------|----------|----------|----------|--------------|-------------|
| 62.2 | 17.9 | 19.9 | 146.6 | <i>p</i> | |
| 49.6 | 11.4 | 39.0 | 182.3 | <i>p</i> | |
| 12.3 | 48.5 | 39.2 | 182.2 | <i>p</i> | |
| 69.6 | 24.1 | 6.3 | 121.7 | <i>o</i> | |
| | | | 104.9 | <i>o-m-p</i> | |

The data (from the same source as in the previous case) on which is based the calculation of the ideal curve, are as follows:

| Substance | Heat of melting (cal.) at <i>t</i> | T_A | K_1 | K_2 | K_3 |
|-----------|------------------------------------|-------|--------|--------|----------|
| <i>o</i> | $3303 + 25.66 t - 0.038 t^2$ | 413.0 | 3.461 | -23.36 | +0.00831 |
| <i>m</i> | $4431 + 5.46 t + 0.018 t^2$ | 426.6 | -2.194 | +2.200 | -0.00393 |
| <i>p</i> | $-1246 + 47.81 t - 0.043 t^2$ | 512.6 | 7.466 | -35.88 | +0.00940 |

⁷ Cf. paper II of this series, in which this correction is discussed in detail.

The ideal values, computed on this basis, together with those interpolated on a large scale curve at a series of values of $1000/T$, are given in Table VII. It also contains results interpolated from Holleman's data on the three systems with benzoic acid as second component; these show that the behavior in these three cases is very little different from the three pairs of chlorobenzoic acids, differing little from the ideal.⁸ Indeed the agreement is in all probability considerably better for the systems with benzoic acid than is indicated by the figures in Table VII; for, to be strictly comparable with ours, they should be raised by 1-1.5%. The basis for this statement is that Holleman's results on the pairs of chlorobenzoic acids (which he also investigated) are lower by 1-1.5% (and, it may be added, somewhat less regular) than ours; the higher temperatures recorded by him for a given mixture are largely due, presumably, to a difference in method of experiment.

TABLE VII
Solubility of the Chlorobenzoic Acids, in terms of C_A (mol percentage of solute) at even intervals of $1000/T$

| | | (a) A = <i>ortho</i> | | | | | |
|---------------------------|---------------|----------------------|-------|-------|-------|-------|-------|
| | | 2.45 | 2.50 | 2.55 | 2.60 | 2.65 | |
| Solvent | $1000/T$ t | 135.1 | 126.9 | 119.1 | 111.5 | 104.3 | |
| Ideal | | 91.6 | 78.7 | 68.0 | 58.8 | 51.0 | |
| <i>m</i> | | 90.9 | 77.7 | 66.6 | 57.1 | | |
| <i>p</i> | | 90.4 | | | | | |
| benzoic acid ⁹ | | 89.0 | 75.3 | 64.0 | 54.9 | 47.3 | |
| | | (b) A = <i>meta</i> | | | | | |
| | | 2.35 | 2.40 | 2.45 | 2.50 | 2.55 | 2.60 |
| Solvent | $1000/T$ t | 152.5 | 143.6 | 135.1 | 126.9 | 119.1 | 111.5 |
| Ideal | | 97.7 | 85.4 | 74.4 | 64.7 | 56.6 | 49.5 |
| <i>o</i> | | 97.9 | 83.2 | 71.8 | 62.4 | 54.7 | 47.9 |
| <i>p</i> | | 97.5 | 83.0 | | | | |
| benzoic acid ⁹ | | 95.5 | 81.0 | 68.8 | 58.4 | 49.6 | 42.1 |
| | | (c) A = <i>para</i> | | | | | |
| | | 2.00 | 2.10 | 2.20 | 2.30 | 2.40 | |
| Solvent | $1000/T$ t | 226.9 | 203.1 | 181.4 | 161.7 | 143.6 | |
| Ideal | | 82.9 | 58.2 | 42.3 | 31.8 | 24.7 | |
| <i>o</i> | | 81.0 | 54.8 | 37.3 | 26.3 | 19.0 | |
| <i>m</i> | | 81.4 | 56.5 | 40.8 | 29.8 | 22.0 | |
| benzoic acid ⁹ | | 83.8 | 57.6 | 39.5 | 27.2 | 18.7 | |

⁸ The divergence in the case of *para* between ideal and experimental is probably due to an error in its heat of melting, this in turn being due to some decomposition at its melting temperature, which is relatively high (239.5°).

⁹ Interpolated from the data of Holleman, (Rec. Trav. chim. 31, 244 (1912)), on the basis of the melting temperature as given by him. This is not a strictly logical mode of comparison, but is however the least arbitrary.

Comparison of the observed eutectic temperature with that extrapolated from the solubility curves shows that here again the latter is slightly higher.

| Components | | Eutectic Temperature | | Eutectic Composition | |
|------------|----------|----------------------|--------------|----------------------|----------------|
| 1 | 2 | Observed | Extrapolated | C ₁ | C ₂ |
| <i>o</i> | <i>m</i> | 108.7 | 109.0 | 54.2 | 45.8 |
| <i>o</i> | <i>p</i> | 131.8 | 131.8 | 84.7 | 15.2 |
| <i>m</i> | <i>p</i> | 140.0 | 140.5 | 79.2 | 20.8 |

In the ternary mixtures the temperatures observed lie close to those calculated for the same percentage, in binary mixture, of the substance which is the stable solid phase. The composition of the ternary eutectic is about 48.3% *ortho*, 44.0% *meta*, 7.7% *para*.

Some Cases of Crystal Miscibility

In an earlier paper it was remarked that solid solution apparently does not occur to any appreciable extent as between the three position isomers C₆H₄XY. This statement, the validity of which is extended by the data just presented, implies that the crystallographic units of these three substances are unlike; as indeed one would expect, except possibly when X is a group large enough to dwarf the importance of the ring. Presumably therefore the occurrence of mix-crystals as between the pairs of components C₆H₄XY and C₆H₄XZ is limited to the cases in which the relative position of the substituents is the same; in other words, we shall not with this type of compound find mix-crystals except we are dealing with a pair of *ortho*, or of *meta*, or of *para* compounds. Even in this case it is to be expected that solid solution would be complete only when the groups Y and Z are very similar (e.g. both halogens) but would extend over a narrower and narrower range with increasing disparity of Y and Z. Indeed our data on the like pairs in the dinitrobenzene-nitroaniline systems show that the groups NO₂ and NH₂ are in this respect so unlike that there is no appreciable mutual solid solubility. The scarcity of relevant experimental data led us to make a few observations, more or less preliminary in character, which indicate that there is complete crystal miscibility between like pairs of the chloronitrobenzenes-bromonitrobenzenes, but incomplete miscibility between *p*-nitrobenzoic acid and *p*-toluic acid.

The primary freezing temperature (t_L) was observed visually as that at which the last crystal disappeared when the temperature of the system was raised very slowly; equilibrium throughout the sample (the weight of which was from 0.2-0.4 gram) was assured by the reciprocating acting of a mechanical stirrer which included the thermoelement, a single junction of #36 constantan and of #40 copper. These observations are, it is believed, accurate to $\pm 0.2^\circ$. The secondary freezing temperature was derived from observation of the break on a controlled heating curve; in this case, owing to poor heat conduction through the solid mass, the accuracy is less good—of the order $\pm 0.3-0.5^\circ$.

The Chloronitrobenzene-Bromonitrobenzene Pairs

The *meta* pairs had previously been investigated by Küster¹⁰ and later by Hasselblatt,¹¹ with concordant results; we worked therefore only with the *ortho* and *para* pairs. Subsequent to the completion of the work it was found that one of the substances in each pair had not been purified sufficiently to make the numerical results of absolute significance; consequently they are not reproduced here. They indicate very clearly however that there was complete miscibility (of type I) as between the samples investigated, in harmony with the previous results on the *meta*-pair. It will be interesting to ascertain if in all cases of this type, when one pair forms a complete series of solid solutions, the other two pairs behave similarly. More accurate data on the liquidus and solidus curves, and on the heat of melting of the components, would enable one to make another test of the validity of the van Laar ideal equation¹² for the case of complete solid solution.

The Pair *p*-Toluic Acid-*p*-Nitrobenzoic Acid

The results, presented in Table VIII, show that in this case there is only partial miscibility on either side at the temperature in question. This indicates that in this respect the group CH₃ resembles NO₂ more closely than does NH₂, but that the resemblance is less than that between Cl and Br.

TABLE VIII
Experimental Observations of Mutual Solubility in the System
p-toluic acid (A)-*p*-Nitrobenzoic acid (B)

| Mol % A | t_L | $t' *$ | $t'' *$ |
|---------|-------|--------|---------|
| 100.0 | 179.6 | | |
| 94.9 | 183.7 | 180.4 | |
| 92.3 | 188.0 | 181.3 | |
| 90.9 | — | 183.0 | |
| 87.3 | 197.7 | — | |
| 84.9 | 201.6 | 186.0 | |
| 82.5 | 204.9 | 186.0 | |
| 75.6 | 213.4 | 186.0 | |
| 66.8 | 221.8 | 184.5 | 212.8 |
| 63.8 | 223.7 | 211.4 | |
| 56.7 | 228.4 | 211.6 | |
| 54.2 | 229.7 | 212.7 | |
| 43.7 | 234.0 | 211.2 | 226.1 |
| 37.1 | 236.4 | 232.6 | |
| 18.5 | 239.3 | 238.9 | |
| 0.0 | 239.3 | | |

* t' and t'' are successive breaks observed on the heating curves.

¹⁰ Küster: Z. physik. Chem., 8, 577 (1891).

¹¹ Hasselblatt: Z. physik. Chem., 83, 1 (1913).

¹² van Laar: Z. physik. Chem., 55, 435 (1906); cf. Bowen: Am. J. Sci., 35, 577 (1913); Z. anorg. Chem., 82, 283 (1913).

Summary

Investigation of each of the 30 solubility curves in the 15 possible binary mixtures of the dinitrobenzenes and nitroanilines shows that the curve is in all cases not far from the ideal calculated from the heat of melting; these divergences, though small and in either direction, are real, but bear no obvious relation to any other measured properties of the pair of compounds. There is no appreciable formation of mix-crystals even between those three pairs in which the relative position of the substituents is the same. On the other hand, the three like pairs of the chloronitrobenzenes and bromonitrobenzenes form a complete series of solid solutions; *p*-toluic acid and *p*-chlorobenzoic acid however show only partial mutual crystal miscibility.

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THE VISCOSITY OF SUPERSATURATED SOLUTIONS. I

BY I. K. TAIMNI

It is well known that solutions of most substances can be cooled below their saturation point without crystallization, provided due precautions are taken to prevent the inoculation of the solution with the minutest crystal of the solid present in the solution. But if the process of cooling is continued, a temperature is reached at which the solid phase makes its appearance even though the solution has been protected from introduction of germ crystals from outside. This phenomenon is known as the spontaneous crystallization of supersaturated solutions.

H. A. Miers and Florence Isaac¹ examined supersaturated solutions of some salts like sodium nitrate and sodium chlorate and showed that, corresponding to every concentration of the salt, there was a definite temperature, at which spontaneous crystallization took place. The line joining the temperatures at which solutions of different concentrations crystallized out spontaneously was found to be approximately parallel to the solubility curve of the salt and was called the "supersolubility curve." An examination of the refractive index of the solutions showed that, as each solution was progressively cooled, its refractive index continued to increase, but, at a certain temperature below the solubility temperature, its value reached a maximum and then began to fall. If the solutions were allowed to cool at rest in presence of growing crystals, this fall was gradual; but if it was stirred during the process of cooling, the fall in the value of the refractive index was abrupt and was followed by a shower of crystals. When the values of the temperatures at which the maximum refractive index was attained were plotted against the concentrations of the solutions, a curve identical with the "supersolubility curve" was obtained. The sudden fall in the value of the refractive index was attributed by Miers to the sudden weakening of the solution as a result of the spontaneous formation of a large number of crystal nuclei in the solution which rapidly grow in size and produce the shower of crystals referred to above.

It, therefore, follows from the work of Miers that a definite change takes place at the temperature of spontaneous crystallization, a temperature at which the solution passes from the "metastable" into the "labile" state.

A number of investigators have examined various physical properties of supersaturated solutions with a view to find out whether the solutions undergo some sudden change at the solubility temperature, a change which will manifest itself by the curve—representing the physical property in question—showing a break at the saturation point. Thus C. Heim² examined the electric conductivity and showed that none of the salt solutions examined exhibited

¹ J. Chem. Soc., 891, 413 (1906).

² Ann. Physik Chem., (3) 27, 673 (1886).

any sudden change in their specific resistance as they passed into the supersaturated condition. W. W. J. Nicol¹ examined the specific viscosity of solutions of some salts a few degrees below the solubility temperature, and found that the viscosity curves are perfectly regular at the saturation point, there is nothing to indicate any change in the constitution of the solutions as they pass from the unsaturated into the supersaturated condition. A similar result was obtained by K. Bindel² who examined the specific gravities, specific heats, and heats of solution of supersaturated salt solutions. From the above investigations it is evident that a solution which is progressively cooled undergoes no sudden change in passing through the solubility temperature.

Miers was the first to demonstrate the existence of a second definite critical point in the condition of a cooling solution. The first critical point is, of course, the solubility temperature at which the solution passes from the unsaturated into the "metastable" region, a region in which the introduction of a crystal from outside is necessary to start the process of crystallization. The second critical point is the "supersolubility" temperature at which the solution passes from the "metastable" into the "labile" region, a region in which crystals begin to form and grow spontaneously in the supersaturated solution.

While the curves representing various physical properties remain perfectly regular in passing through the solubility temperature, Miers found that the refractive index curves of solutions passed through maxima at their respective supersolubility temperatures. It was, therefore, expected that an examination of other physical properties of supersaturated solutions might reveal similar irregularities in the curves representing those properties. A physical property suitable for an investigation of this kind is viscosity. The present investigation was undertaken with a view to measure the viscosity of supersaturated solutions. It will be seen that the viscosity curves, as far as they have been traced, remain quite regular. We are, therefore, justified in concluding that the viscosity of a solution undergoes no sudden change below the saturation temperature.

The viscosity measurements were made by means of an apparatus devised by Scarpa³ and used by F. D. Farrow⁴ for measuring the viscosity of soap solutions. It was necessary to introduce certain modifications in this apparatus to prevent the inoculation of the supersaturated solutions with germ crystals carried by dust particles or formed at the margin of the solution through evaporation of the solvent.

The method consists in measuring the time t_1 , taken in drawing up, by suction, a fixed volume of the solution through a capillary tube, and the time t_2 which this volume of the solution takes in flowing out through the capillary tube under the action of gravity.

¹ J. Chem. Soc., 51, 389 (1887).

² Ann. Physik Chem., (3) 40, 370 (1890).

³ Gazz., 40, 271 (1920).

⁴ J. Chem. Soc., 101, 347 (1912).

Given constant conditions, the viscosity of any liquid, according to Scarpa, is proportional to the expression $\frac{t_1 \cdot t_2}{t_1 + t_2}$ (t_2 measured in seconds).

$$\text{or} \quad \eta_{\text{liquid}} = K \times \left(\frac{t_1 \cdot t_2}{t_1 + t_2} \right)_{\text{liquid}}$$

where K is a constant which can be determined by calibrating the apparatus with water.

The great advantage of this method over the ordinary method lies in the fact that it is not necessary to measure the density of the liquid. It is extremely difficult to avoid the inoculation of a supersaturated solution with germ crystals in the process of the density determination, and hence the ordinary method which requires a knowledge of the density of the solution at each temperature is practically inapplicable in the case of supersaturated solutions.

The work of numerous investigators has shown that the crystallization of a supersaturated solution is brought out by germ crystals introduced from outside. Provided the vessel containing the solution has been properly cleaned and the substance has been completely dissolved, the inoculation of the solution with germ crystals can take place either through the dust particles suspended in the atmosphere, or through evaporation of the solvent and the consequent deposition of minute crystals at the margin of the solution. Modifications were, therefore, introduced into Scarpa's apparatus to guard against the inoculation of the solutions in either of these ways, and it was thus found possible to cool the solutions far below their respective solubility temperatures. Of course, in some cases, crystallization took place, owing to the formation of a few nuclei in the solution itself, but even in such cases, the crystallization was so slow that it was possible to determine the viscosity of the solution at temperatures some degrees below the temperature of spontaneous crystallization.

The viscometer and the accessory apparatus used are shown in Fig. 1. A is a cylindrical glass vessel with a side tube F. The mouth of the vessel is fitted with a rubber stopper through which passes a glass tube G connected at its lower end with a viscometer consisting of a bulb B to which a capillary tube C is attached. The glass tube G can be put into communication with the aspirator H and thus suction applied to fill the bulb of the viscometer with the solution contained in the vessel A. The suction exerted depends on the difference of water level in the aspirator H and the beaker placed underneath, and its value is measured by means of the water manometer M. Before connecting the aspirator H with the viscometer, the pressure is always brought to a constant value—3.0 cm—by adding to or withdrawing water from the beaker. The difference in the manometer reading before and after each reading of time is not greater than *one* millimeter and thus the pressure remains practically constant during the process of filling the viscometer bulb.

The U-tubes D and E are connected with the two-way tap T which puts one or the other of the U-tubes into communication with the air contained in

the aspirator S. The mouth of this aspirator is fitted with a rose for producing a fine spray of water. This spray removes all the dust particles from the air contained in the aspirator, and thus all the air coming into contact with the surface of the supersaturated solution is free from crystal germs, which if present will bring about the release of supersaturation even in the "metastable" region. It is not possible to purify the air by passing it through water as this would disturb the pressure.

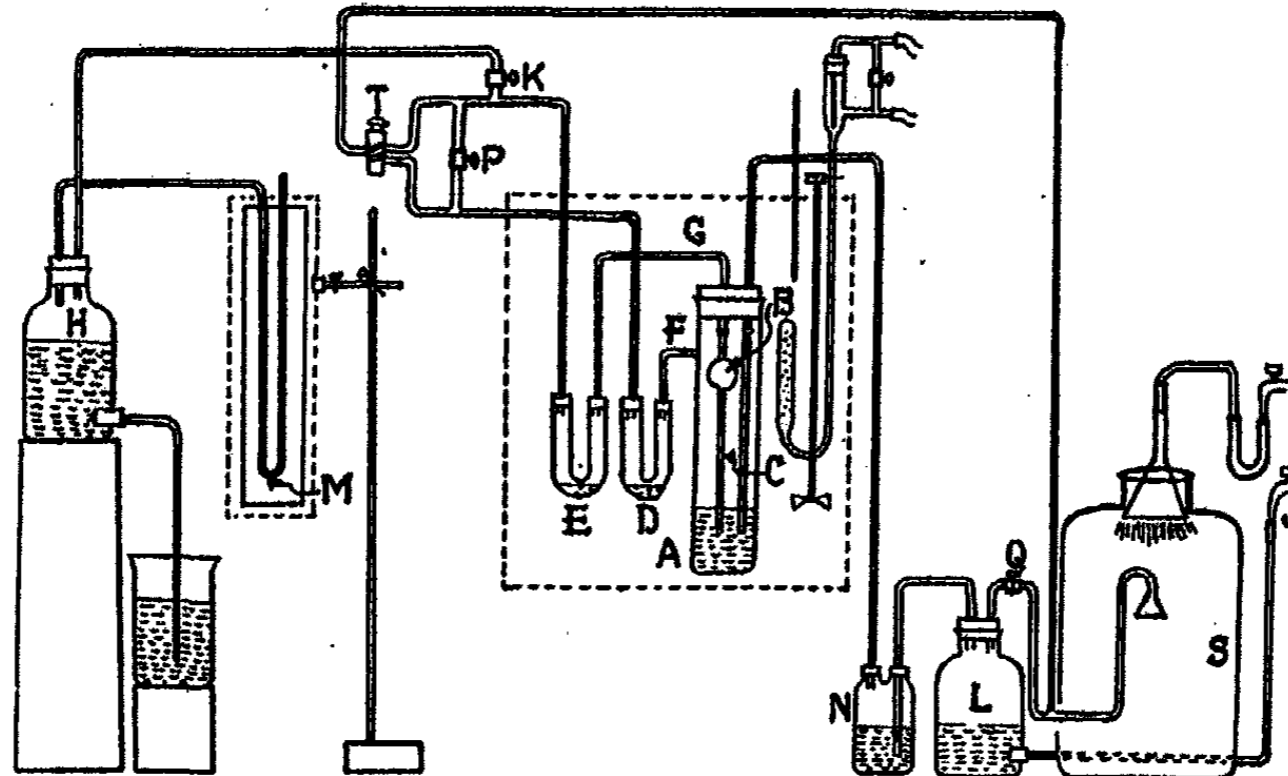


FIG. 1
Apparatus for measuring Viscosity of Supersaturated Solutions

When the solution is to be sucked up into the bulb of the viscometer, the tap T is turned so as to put the U-tube D into communication with the air in the aspirator S, the clip at P is closed, and suction applied by opening the clip at K. When the bulb is to be emptied the clip at K is closed, and both the U-tubes are simultaneously put into communication with the air in the aspirator S, by turning the tap T and opening the clip at P.

Both the U-tubes contain a small quantity of water which serves to maintain a vapour pressure at the surface of the solution higher than the vapour-pressure of the solution itself. This prevents any evaporation of the solvent from the surface of the solution and the consequent formation of minute crystals near the margin of the solution. Theoretically, water should distil from the U-tubes, into the solution and decrease its concentration but in practice the quantity of water so carried over is so small as to be negligible.

The aspirator L and the wash-bottle N serve to pass a current of dust-free air through the whole apparatus when necessary. This sweeps away any dust particles that may be hanging in the air enclosed within the apparatus. After closing the clip at Q, water is made to flow into the aspirator L from the tap J. The air in the upper part of the aspirator is forced out, and after being washed in the Wolff's bottle N, is made to circulate through the whole apparatus and then ejected into the aspirator S. When the aspirator L becomes full with

water, the clip at Q is opened and water made to flow out through the opening near the bottom of the aspirator. Purified air from the aspirator S fills the aspirator L and can be circulated through the aspirator as before.

The parts of the apparatus surrounded by a dotted line are enclosed in a gas-heated water thermostat with glass sides. For temperatures below the room temperature iced water was added from time to time as required.

As solutions of widely different viscosity were investigated, it was necessary to use viscometers with capillary tubes of different radii. With a particular solution, that viscometer was used which made the time of flow convenient to measure. Three viscometers were used but as these were calibrated with water, it was not considered necessary to measure their essential dimensions.

For convenience sake, values of the expression $\frac{(t_1 \cdot t_2)}{(t_1 + t_2)}$ are plotted against temperature. The absolute viscosity is proportional to this expression and can be obtained by multiplying the expression by the "viscosity factor" given with each curve. The value of this "viscosity factor" was obtained by alibrating the particular viscometer used with water. As the value of the expression $\frac{(t_1 \cdot t_2)}{(t_1 + t_2)}$ varies to a slight extent with the height of the liquid in the vessel A, the "viscosity factor" gives only approximately the absolute viscosity. The relative value of the viscosity for each solution is, however, correctly given by the expression $\frac{(t_1 \cdot t_2)}{(t_1 + t_2)}$ because the height of the solution remains constant throughout one series of experiments.

In carrying out an experiment, a solution of known concentration was prepared by introducing a weighed quantity of the substance into a small flask and adding a measured quantity of water. The mouth of the flask was closed with a rubber stopper which was made quite secure in its place by means of a piece of string. The flask was heated in boiling water till all the solid had gone into solution. The rubber stopper was then removed from the flask and the solution—still much above its solubility temperature was carefully transferred to the bottom of the vessel A with the help of a piece of glass tubing. The rubber stopper carrying the viscometer was carefully replaced, the whole apparatus was lowered well beneath the surface of water in the thermostat, and after adjusting the viscometer in a vertical position, the solution was allowed to attain the constant temperature of the thermostat. The times taken in the ascent and descent of the solution were measured by means of a stop watch, several readings being taken for each temperature.

The times of ascent and descent of the solution are influenced by the temperature and the pressure, and experiments were therefore made to determine roughly the extent to which a slight error in the measurement of these affected the time of ascent or descent. It was found that a difference of pressure of 1 cm altered the time of ascent by about one per cent. The error in the measurement of pressure which could at most be .5 mm, could not, therefore affect

the time of descent by more than .05%. The effect of slight error in the measurement of temperature depended to a very great extent on the nature of the solution whose viscosity was being measured, but even in the case of those solutions whose viscosity was greatly affected by change of temperature, an alteration of .05°C did not affect the time of ascent or descent by more than .5%.

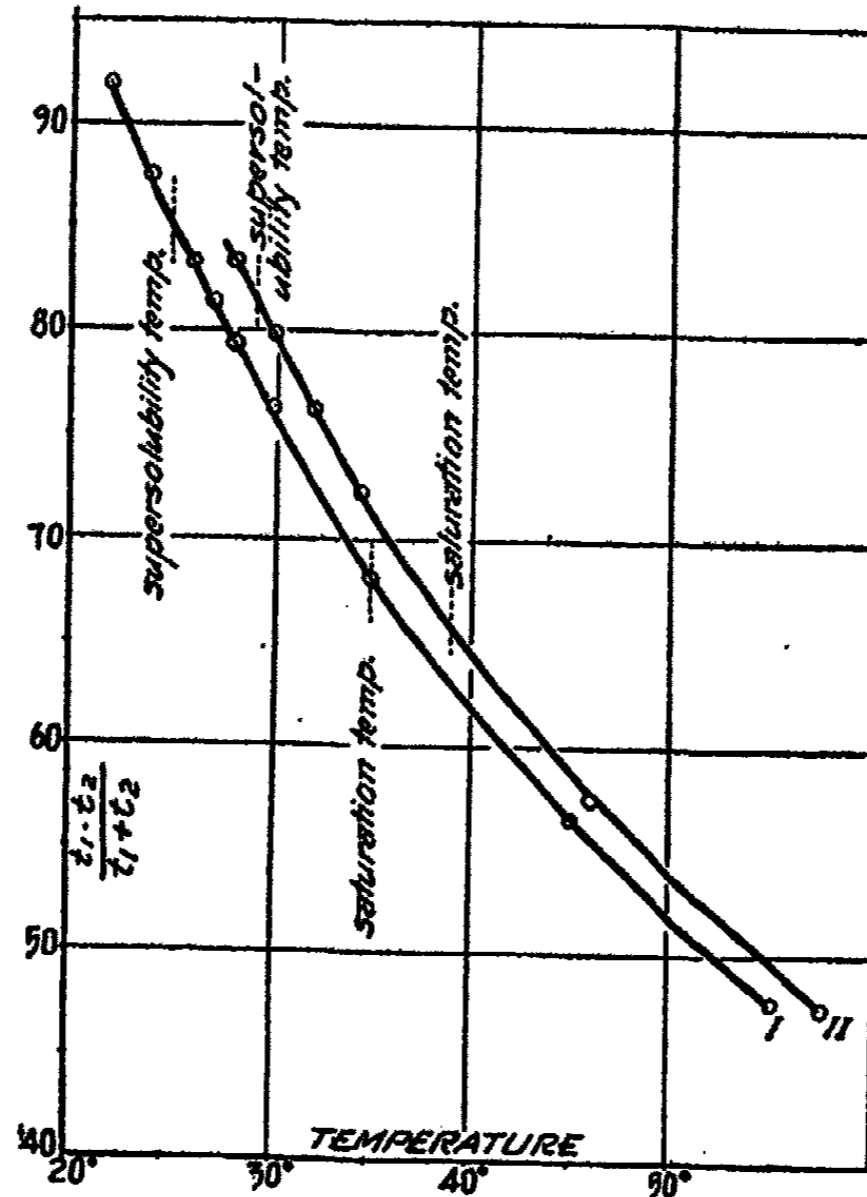


FIG 2.

Viscosity of Sodium Nitrate Solutions
 I. Solution contains 50% Salt
 II. Solution contains 51% Salt
 Viscosity Factor 33×10^{-4}

Solutions of six substances—sodium nitrate, sodium chlorate, copper sulphate, sodium thiosulphate, tartaric acid and cane sugar—were examined. Two solutions of different concentrations were investigated in the case of each substance, in order to obtain an approximate idea of the effect of change of concentration on the viscosity of the solution.

Sodium Nitrate, Sodium Chlorate and Copper Sulphate

The curves in Figs. 2 and 3, which are very much alike, show the change of viscosity with falling temperature for solutions of sodium nitrate and sodium chlorate. It will be seen that the curves remain quite regular in pass-

ing through the temperature of spontaneous crystallization as determined by Miers. It was not possible to measure the viscosity at temperatures very much below the temperature of spontaneous crystallization, because, when the solutions were cooled a few degrees below this temperature, minute crystals began to appear in the solution and ultimately blocked the capillary tube. In no case did the crystals make their appearance in the "metastable" region, but only after the solution had been cooled a few degrees below the tempera-

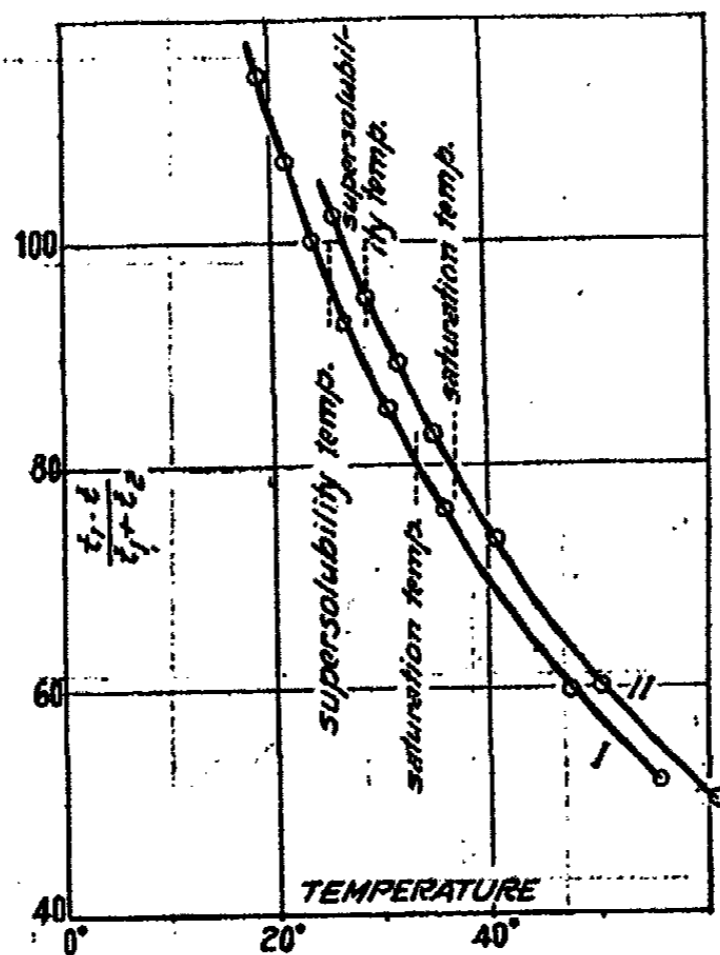


FIG. 3
Viscosity of Sodium Chlorate Solutions
I. Solution contains 53.4% Salt
II. Solution contains 54.4% Salt
Viscosity Factor 33×10^{-5}

ture of spontaneous crystallization. It follows, therefore, that the appearance of crystals was due to spontaneous formation of crystal nuclei in the solution itself and not to the introduction of germ crystals from outside.

The curves in Fig. 4 for copper sulphate solutions are similar to those obtained for sodium nitrate and sodium chlorate, except that the solutions could be cooled much below the solubility temperature before crystals began to appear in the solution. While in the case of sodium nitrate and sodium chlorate solutions spontaneous crystallization took place roughly about 10 degrees below the saturation temperature, in the case of copper sulphate solutions, the first crystal did not form until the temperature of the solution had been reduced 30° - 40° below the saturation point. No definite supersolubility data were available, but the curves, as far as they could be traced remained perfectly regular.

Sodium Thiosulphate, Tartaric Acid and Cane Sugar

The curves for these substances are given in Figs. 5-7 and differ in some ways from the preceding curves. Not only is the initial viscosity very much greater than in the case of the preceding three substances, but it also increases very rapidly as the temperature is lowered. For example, the viscosity of 66% tartaric acid solution at 10° is almost double that at 20° and the viscosity of 75% cane sugar solution at 16° is almost three times that at 26°.

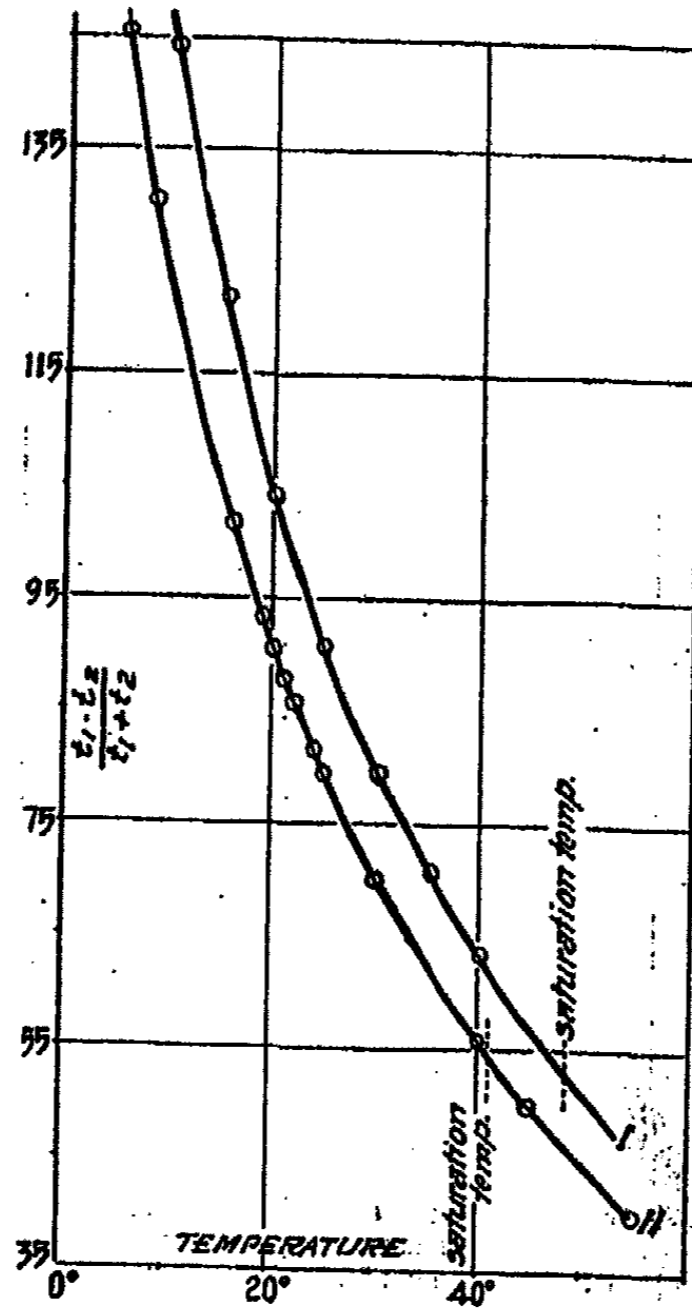


FIG. 4
 Viscosity of Copper Sulphate Solutions
 I. Solution contains 38.3% hydrated Salt
 II. Solution contains 35.1% hydrated Salt
 Viscosity Factor 33×10^{-5}

Another peculiarity in the case of these substances is the divergence of the two curves representing two different concentrations of the same substance. This means that the difference in viscosity of the two solutions becomes greater and greater as the temperature is lowered. In the case of sodium thiosulphate solutions, the difference at 60° is about 5 units and at 5° about 35 units. In the case of tartaric acid solutions, the difference at 60° is about 10 units and

at 10° about 200 units. In the case of cane sugar, the difference at 60° is about 20 units and at 15° it reaches the remarkable value of about 1350 units.

Although solutions of these substances were cooled 30°-45° below their respective solubility temperatures, no sign of spontaneous crystallization was

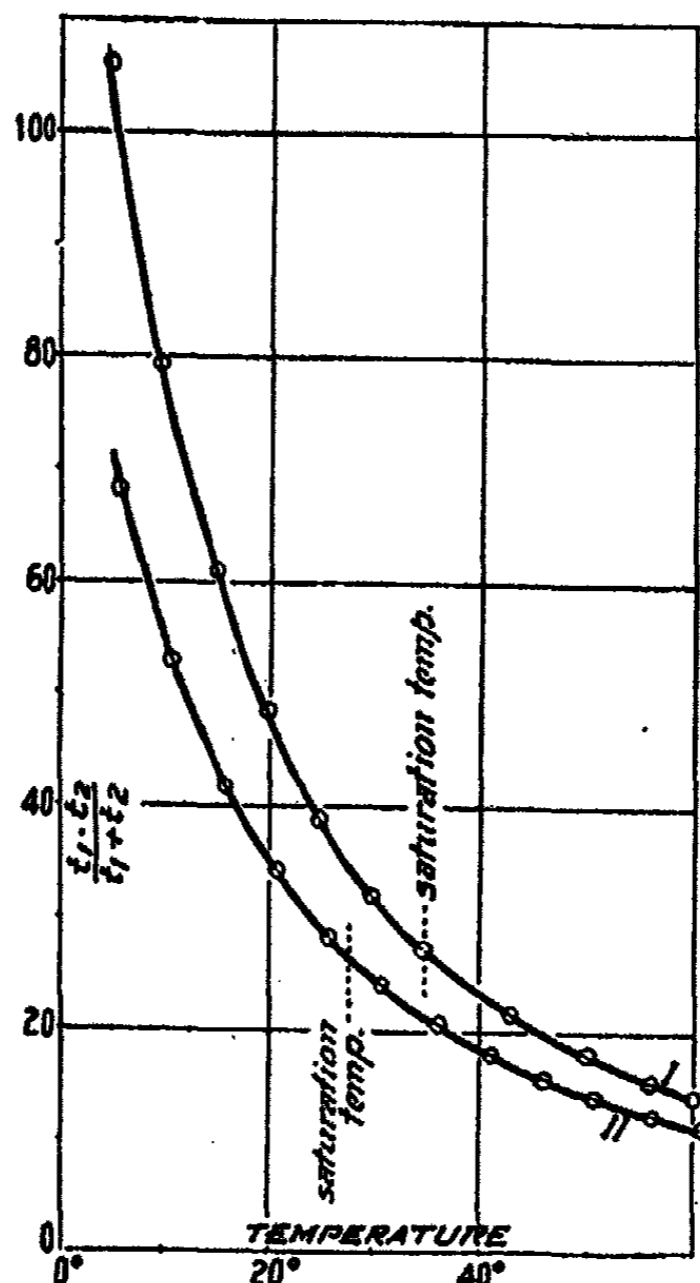


FIG. 5
Viscosity of Sodium Thiosulphate Solutions
I. Solution contains 75% hydrated Salt
II. Solution contains 70% hydrated Salt
Viscosity Factor 24×10^{-4}

obtained. In some cases, after finishing the viscosity measurements, the solutions were placed in a freezing mixture of ice and salt, but even then no crystallization took place.

The present investigation was primarily undertaken with the object of finding out whether the viscosity curves of cooling solutions suffer any marked change in passing through their respective supersolubility temperatures. Supersolubility data were available only in the case of two substances, sodium nitrate and sodium chlorate. Viscosity curves for solutions of these substances show no break in passing through the supersolubility temperatures as

determined by Miers. In the case of the other four substances, supersolubility data were not available, but the viscosity curves remain quite regular even 30° – 45° below the saturation temperatures.

Of these four substances, solutions of only one, namely copper sulphate, exhibited anything like the phenomenon of spontaneous crystallization

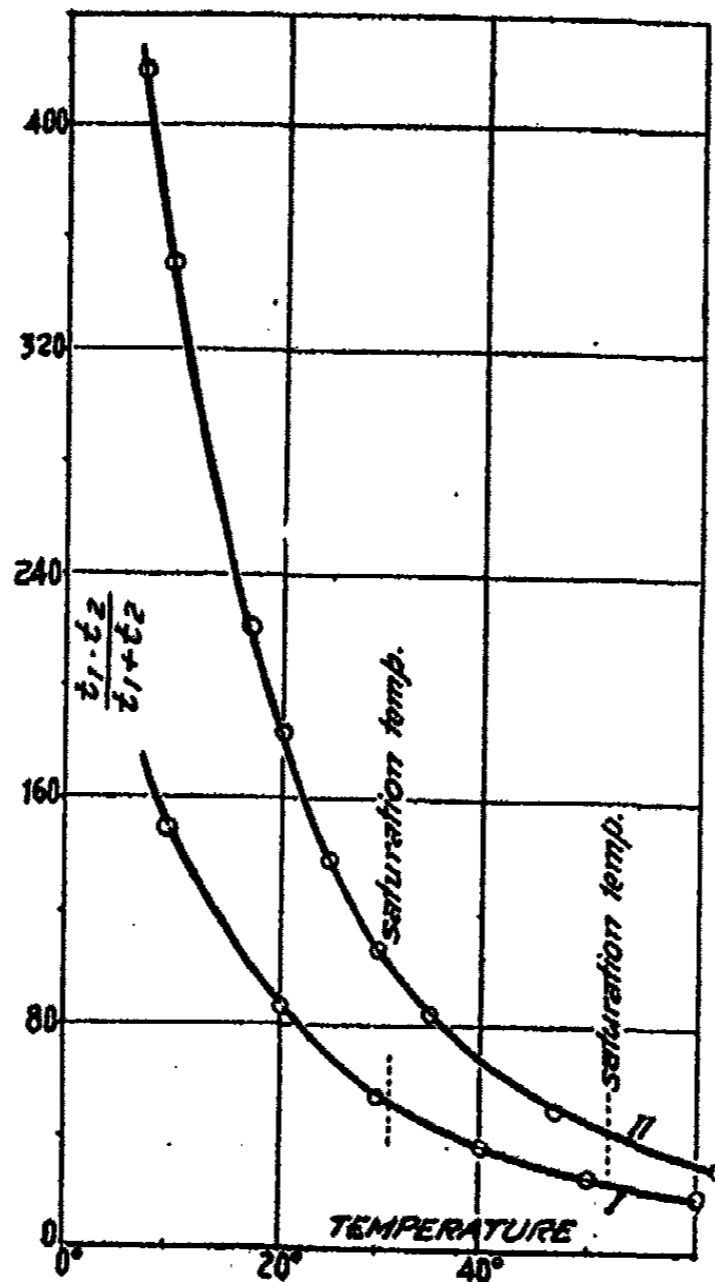


FIG. 6
Viscosity of Tartaric Acid
I. Solution contains 61.2% Acid
II. Solution contains 66.6% Acid
Viscosity Factor 24×10^{-4}

minute crystals making their appearance in the highly supersaturated solution at sufficiently low temperatures. In the case of sodium thiosulphate, tartaric acid and cane sugar solutions, there was no sign of spontaneous crystallization. Either the solutions of these substances do not show the phenomenon of spontaneous crystallization at all, or the lowest temperatures reached were still above their supersolubility temperatures. This inability on the part of these highly supersaturated solutions to crystallize out spontaneously may be attributed to the high viscosity of the liquid, on account of which the nuclei

formed in the solution take a very long time to attain the size at which they become visible. This latter explanation does not, however, seem to be tenable, at least in the case of sodium thiosulphate solutions, which in spite of being very viscous at low temperatures, crystallized out immediately on inoculating the solutions with a minute crystal of the salt.

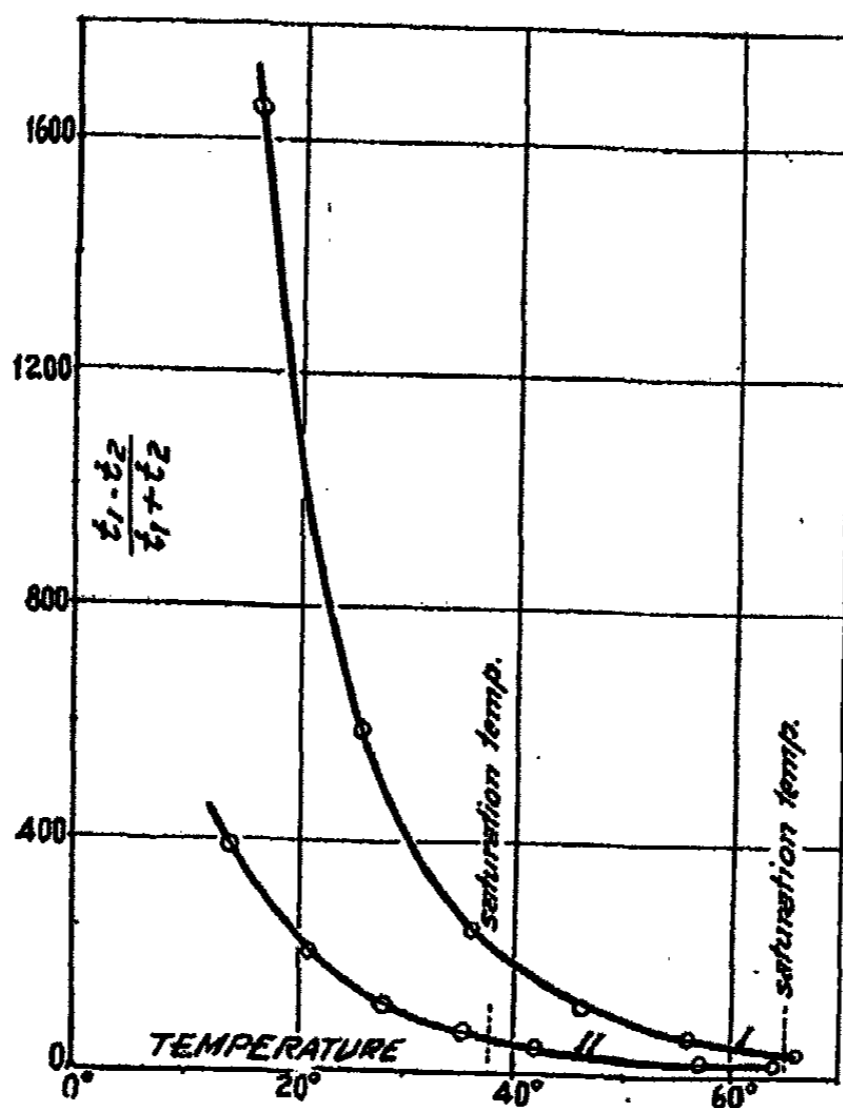


FIG. 7
Viscosity of Cane Sugar Solutions
I. Solution contains 75% Sugar
II. Solution contains 70% Sugar
Viscosity Factor 22×10^{-3}

Summary

(1) Viscosities of supersaturated solutions of six substances—sodium nitrate, sodium chlorate, copper sulphate, sodium thiosulphate, tartaric acid, and cane sugar—have been determined by means of an apparatus devised by Scarpa, and modified by the author in a suitable manner for measuring the viscosity of a supersaturated solution.

(2) It has been shown that the viscosity curves, in the case of sodium nitrate and sodium chlorate solutions remain quite regular not only in passing through the saturation temperature but also in passing through the temperatures of spontaneous crystallization as determined by Miers.

The refractive index curves of these solutions, according to Miers, pass through maxima at the temperatures of spontaneous crystallization. In the

case of the other four substances examined, no 'supersolubility' data are available but the viscosity curves, as far as they could be traced, (30° - 45° below the saturation temperature) remained perfectly regular.

(3) Out of the four substances, only one, viz: copper sulphate, exhibited the phenomenon of spontaneous crystallization at sufficiently low temperatures. In the case of sodium thiosulphate, tartaric acid and cane sugar solutions there was no sign of spontaneous crystallization even when the temperature was lowered 30° - 45° below the saturation temperature.

I desire to express my thanks to Professor Donnan for his helpful criticism and valuable advice during the course of this investigation.

*The Sir William Ramsay Laboratories of Physical and Inorganic Chemistry,
University College, London,
December 19, 1927.*

AN EXAMINATION OF PATRICK'S THEORY OF ADSORPTION

BY SIDNEY J. GREGG

Much interesting material has been put forward recently by Patrick and his co-workers, which is regarded as supporting the capillarity theory of adsorption proposed in 1920 by Patrick and McGavack.¹ The present author's investigation² of the adsorption of gases by charcoal led him to examine along with other theories of adsorption, that of Patrick and McGavack, and the result of this examination is detailed below.

Patrick assumes that adsorption is due to condensation of the vapour to the liquid state in the capillaries of the adsorbent, the necessary reduction in vapour pressure occurring in consequence of the sharp concavity of the liquid meniscus. The true measure of pressure will therefore be the "relative pressure" p/p_0 , where p is the equilibrium pressure of the adsorbed vapour, and p_0 its saturated vapour pressure at the temperature of experiment; the amount of substance adsorbed should be expressed, not in weight, as is customary, but in terms of its liquid volume, which must however be corrected for the fact that it is expanded owing to the negative hydrostatic pressure exerted by the meniscus. This correction Patrick empirically assumes to be given by introducing the surface tension of the liquid as a correction-factor, since in some cases the relationship $\beta\sigma^{1/2} = \text{a constant}$, is known to hold between the surface tension σ and the compressibility β of liquids. Since the corrected volume adsorbed at a given relative pressure p/p_0 , should be independent of the nature of the adsorbed substance and of temperature, Patrick arrives at the formula

$$V = K \left(\frac{p\sigma}{p_0} \right)^{1/N}$$

where V is the amount of substance adsorbed expressed as volume of liquid, per gram of adsorbent, and K and $1/N$ are constants for a given adsorbent, no matter what the temperature or the substance adsorbed.

Hence on plotting $\log V$ against $\log p\sigma/p_0$, all points for a given adsorbent should fall on the same straight line, independent of temperature and nature of adsorbed substance.

The first case examined by Patrick,³ viz. the adsorption of sulphur dioxide by silica gel at temperatures from -80° to 100° , fulfills this condition fairly well, though the present author has found that the best line through the points is not quite straight.

But the question arises, is surface tension the only quantity which will cause coincidence of the otherwise widely separated $\log V - \log p/p_0$ curves for

¹ Patrick and McGavack: J. Am. Chem. Soc., 42, 946 (1920).

² J. Chem. Soc., 1927, 1494.

³ Patrick and McGavack: loc. cit.

different temperatures? Since adsorption falls off with rise of temperature, any quantity which also decreases with rising temperature, will, like σ , bring the curves closer together. If, for instance, the simple quantity $1/T$ be employed (where T is absolute temperature) and $\log p/p_0 T$ be thus plotted against $\log V$ for the above experiment, the curves for the different temperature are brought closer together, though the degree of coincidence is not so good as Patrick's.

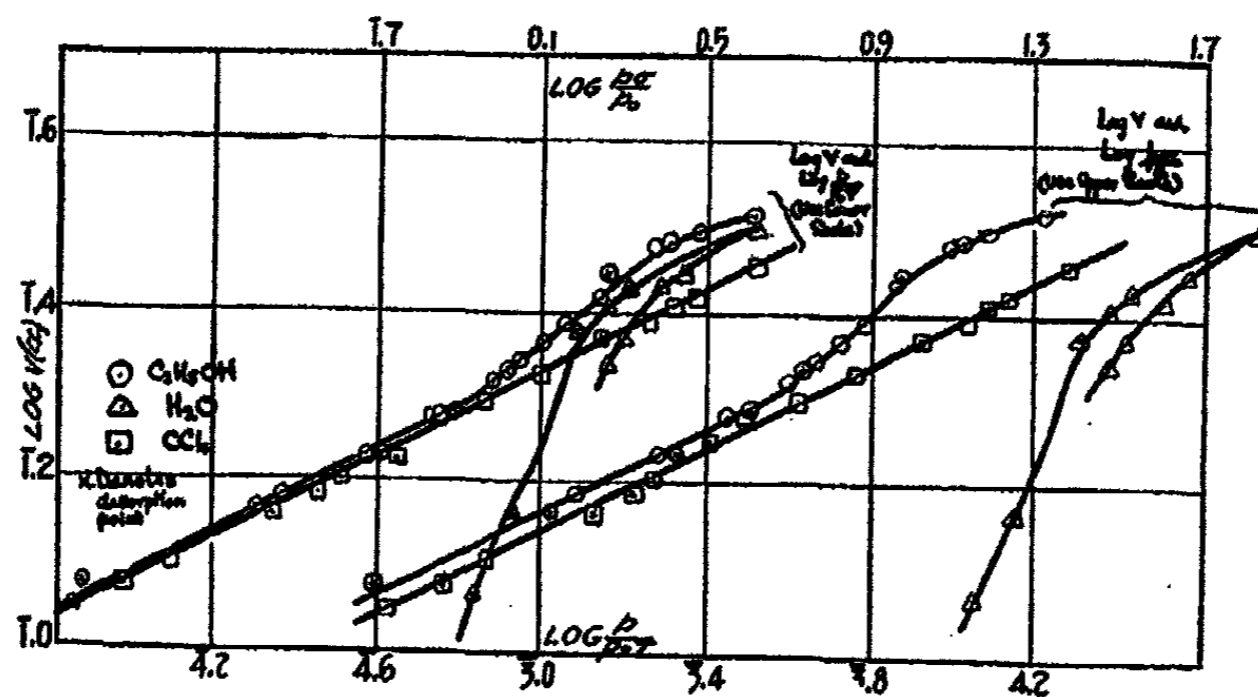


FIG. 1
Plot of $\log V$ against $\log \frac{p}{p_0 T}$ and $\log V$
against $\log \frac{p\sigma}{p_0}$ for C_2H_5OH , CCl_4 and H_2O .

On applying the same treatment to the data for butane¹ at 0° , 20° and 30° , it is found that equally good results are obtained with either σ or $1/T$; similarly with ammonia, an equally good degree of coincidence is obtained with either quantity, though in both cases the best line through the points is not quite straight, showing that they do not fit accurately an equation of the Partick type.

When Patrick's formula is applied to his measurements² for ethyl alcohol, carbon tetrachloride and water vapour on silica gel, one curve (that for water) still remains widely divergent from the others; whereas on plotting $\log p/p_0 T$ instead of $\log p\sigma/p_0$, a considerably greater degree of coincidence is obtained (Fig. 1). This throws much doubt on the validity of Patrick's formula, in spite of his special explanation for the position of the water curve; he points out that in this experiment the water was slow in attaining equilibrium, and moreover exhibited hysteresis (i.e. the sorption and desorption curves did not coincide) which indicates that the equilibrium was not a true one. This he explains by the fact that the viscosity of water below 30° , unlike that of most other substances, increases with fall of pressure, so that owing to the large

¹ Patrick and Long: *J. Phys. Chem.*, 29, 336 (1925).

² Patrick and Opdycke: *J. Phys. Chem.*, 29, 601 (1925).

negative hydrostatic pressure exerted by the meniscus, the viscosity is increased. This increases the time required for the attainment of equilibrium so that the time occupied by the water measurements was not long enough for true equilibrium to be reached.

That this explanation is unlikely is shown by the following considerations: the magnitude of the negative pressure on the liquid at 30° when $p = 0.1$ mm., say, (calculating according to the Gibbs' formula quoted by Patrick¹) is 130

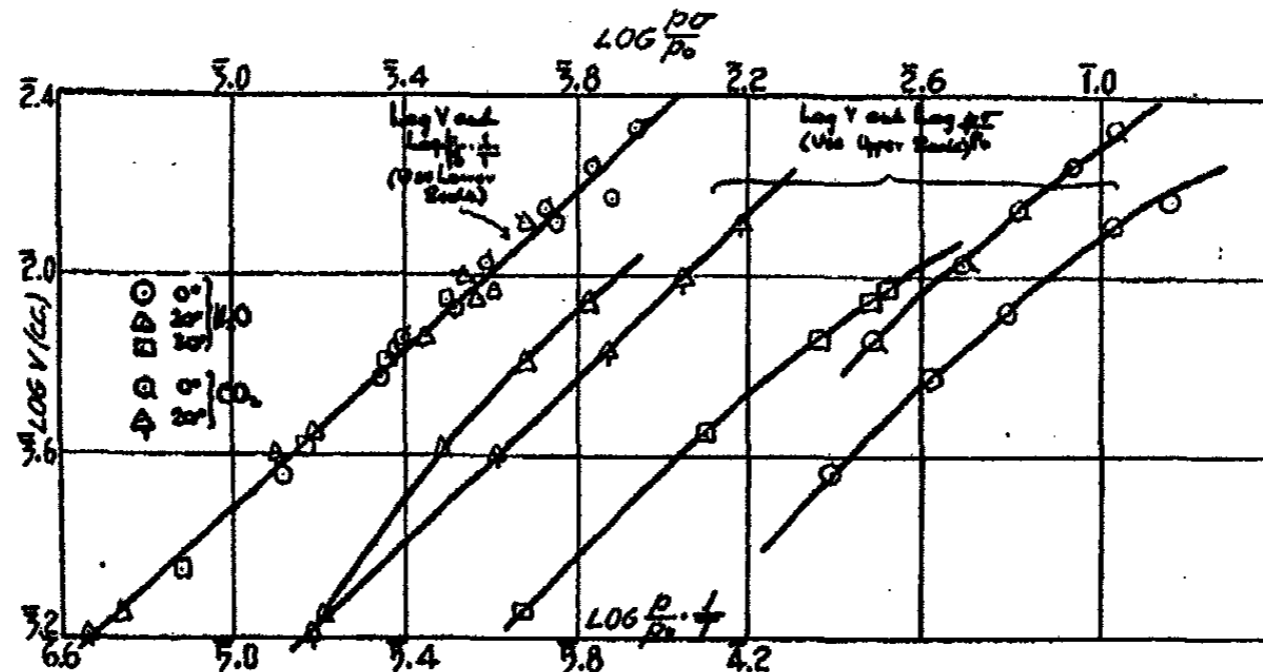


FIG. 2

Plot of $\text{Log } V$ against $\text{Log } \frac{P}{p_0 T}$ and $\text{Log } V$ against

$\text{Log } \frac{P\sigma}{p_0}$ for CO_2 and N_2O .

atmospheres, which would give rise to a viscosity change of less than 0.3% (Cohen: "Piezochemie," p. 259). It is difficult to believe that this small change in viscosity could have such a large effect on the rate of movement of water, for this movement would no doubt be analogous to flow through a capillary tube, the velocity of which decreases in a linear manner with increasing viscosity.

A further case indicating the inadequacy of the Patrick formula, is the adsorption of nitrous oxide and carbon dioxide² by silica at 0° , 20° and 30° , where the plot of $\log V$ against $\log p\sigma/p_0$ gives widely separated curves. (Fig. 2). Again Patrick uses a special explanation, pointing out that according to Freundlich³ the surface tension of a liquid in a concave surface is smaller than in a plane one, this effect becoming appreciable when the radius of curvature is less than 10^{-6} cm.; then by an application of the well-known Kelvin formula for the relationship between the radius of a capillary r , and the vapour pressure over a liquid in the capillary, viz.

$$\log p/p_0 = -2\sigma/Dp_0 r$$

¹ Patrick and McGavack: loc. cit., 975.

² Patrick, Preston and Owens: J. Phys. Chem., 29, 421 (1925).

³ Freundlich: "Kapillarchemie," 63 (1923).

where D and d are the liquid and vapour densities respectively, he obtains the corrected value for the surface tension. This proceeding must be regarded as questionable, however, for the values of r dealt with are of the order 5×10^{-8} cm., i.e. approximately the diameter of a single molecule; and an extrapolation down to molecular dimensions of a formula which is essentially statistical in nature and applies only to a substance in bulk, seems, as indeed Patrick admits elsewhere,¹ scarcely permissible. The unsatisfactory nature of the method, is emphasized by the fact that even after thus correcting, one curve still remains widely divergent. On substituting r/T for σ on the contrary, all the curves come very close together, no further modifications of the formula being necessary. (Fig. 2).

In view of the above examination, there seems little doubt that the Patrick formula is unsatisfactory; the presence in it of the surface tension σ is shown to be unjustified, even the entirely empirical quantity r/T securing for the formula a closer agreement with experimental data. Even when so amended, however, the formula can be regarded only as a purely empirical relationship, which does not provide a basis for a theory of adsorption.

The rejection of Patrick's formula in the form suggested by him does not of course rule out the possibility of capillary condensation, but it shows that the present evidence for Patrick's view is incomplete.

*King's College,
Strand,
London, W. C. 2.,
England,
November 30, 1927.*

¹ Patrick and McGavack; loc. cit., 973.

MOLECULAR ORIENTATION AT SURFACES OF SOLIDS. II. THE
WORK OF ADHESION OF THE SATURATED FATTY ACIDS
FOR WATER*

BY A. H. NIETZ

The method used in calculating the work of adhesion and the measurements upon which it is based have been discussed in the previous paper. In fact the measurements, repeated in Table I, were there recorded without comment and are made the subject of a separate communication here, since they seem to open up new questions.

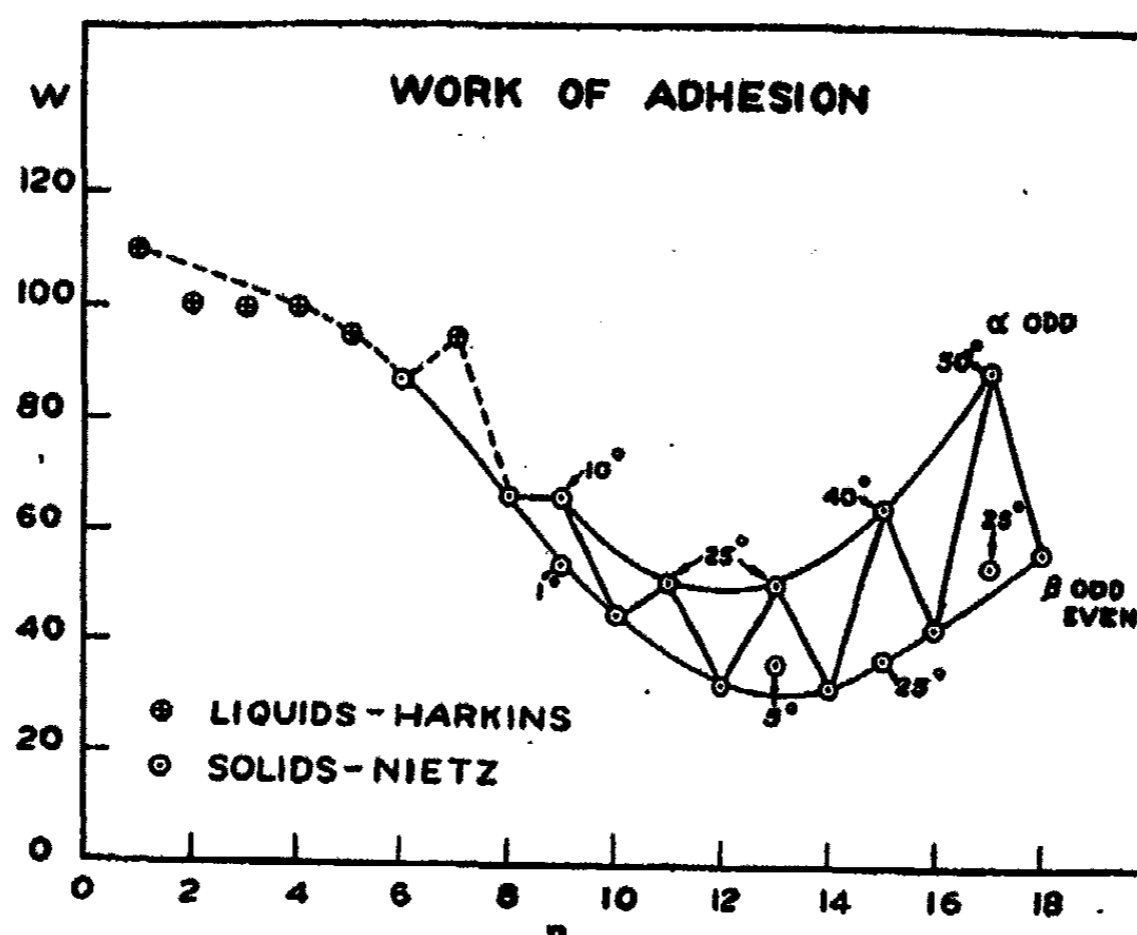


Fig. 1.

TABLE I

| Acids | θ | TR | W | Acids | θ | TR | W |
|---------------------|----------|----|------|-----------------------|----------|----|------|
| Caproic | 45 | 30 | 87.0 | Tridecylic β | 95 | 40 | 36.5 |
| Caprylic | 60 | 38 | 66.2 | Myristic | 115 | 25 | 32.0 |
| Pelargonic α | 49 | 45 | 66.1 | Pentadecylic α | 73 | 31 | 65.0 |
| Pelargonic β | 69 | 45 | 54.0 | Pentadecylic β | 110 | 21 | 37.8 |
| Capric | 85 | 43 | 45.1 | Palmitic | 111 | 6 | 42.8 |
| Undecylic | 79 | 44 | 50.8 | Margaric α | 77 | 0 | 89.0 |
| Lauric | 111 | 31 | 32.6 | Margaric β | 105 | 9 | 54.2 |
| Tridecylic α | 75 | 45 | 50.4 | Stearic | 106 | 0 | 56.8 |

* Communication No. 323 from the Research Laboratory of the Eastman Kodak Company. Read at the Richmond meeting of American Chemical Society.

These measurements are graphically summarized in Fig. 1, in which work of adhesion is expressed as the ordinate and n as the total number of carbon atoms on the horizontal axis. The points in all cases represent averages where more than one determination was made.

It is seen at once that the well-known alternation between the acids of odd and even carbon atoms is very pronounced. The magnitude of the alternation is greater for work of adhesion than it is perhaps for any other physical property. The two enantiotropic forms of the odd acids have been

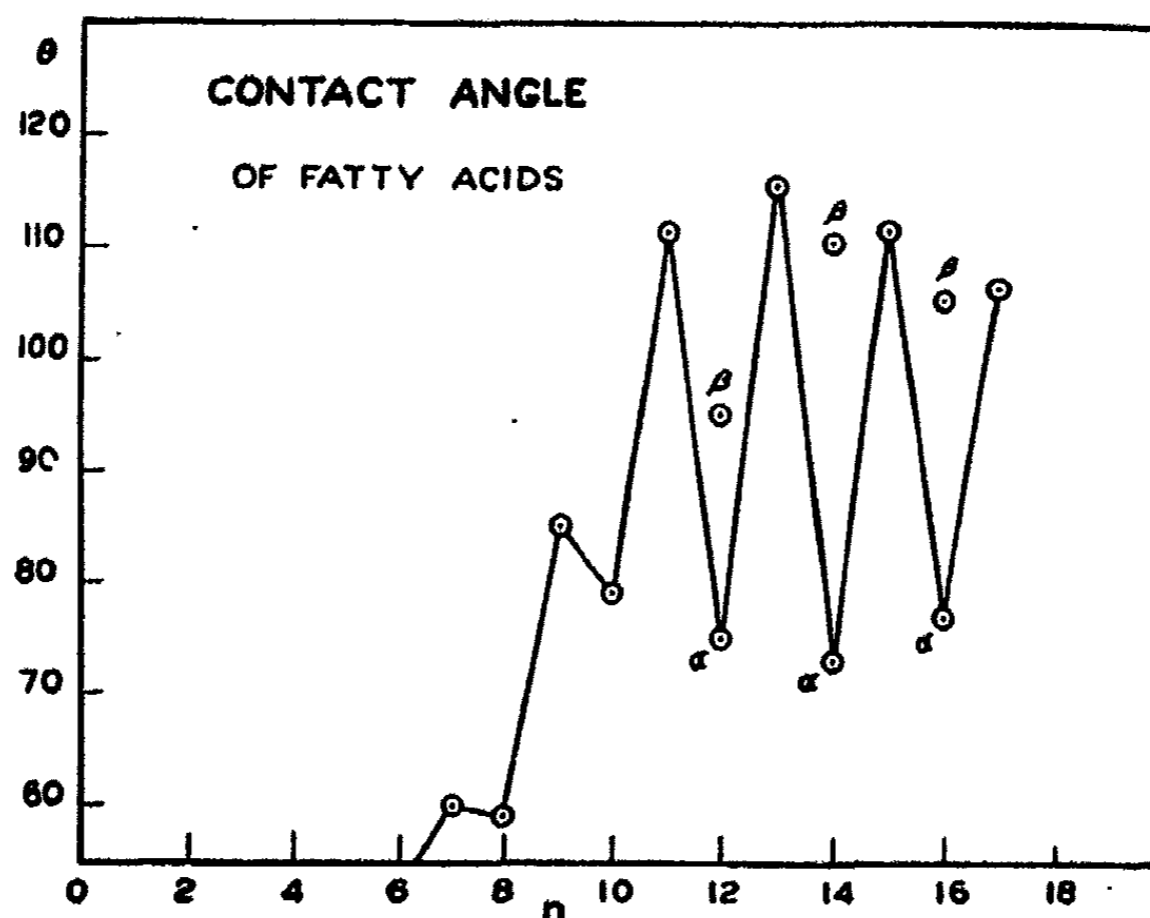


FIG. 2

measured and the results are shown in the figure. The lower curve is for the even acids and the β odd acids fall approximately on this curve, and the upper curve is for the α odd acids. The α odd acids are stable only at temperatures relatively near their melting points. The β odd acids of the higher members are the forms stable at ordinary temperatures. The lower members of the β odd acids are stable only at relatively low temperatures. In order to measure the β form of pelargonic acid (9 carbon atoms) for example, it was necessary to freeze the acid with carbon dioxide snow and to make the measurements very quickly in water as near the freezing point as possible.

In Fig. 2 the detailed values for the contact angle of the acids are shown. It is seen that the extent of alternation exhibited by the odd and even acids is very great. In Fig. 3 the percentage reduction of the surface tension of water is plotted against the number of carbon atoms. Here, also, a certain amount of alternation is evident. It is therefore natural to expect that the values of work of adhesion ($W = T(1 + \cos \theta)$) should show a considerable degree of alternation. In Figs. 4-9 there are summarized most of the existing

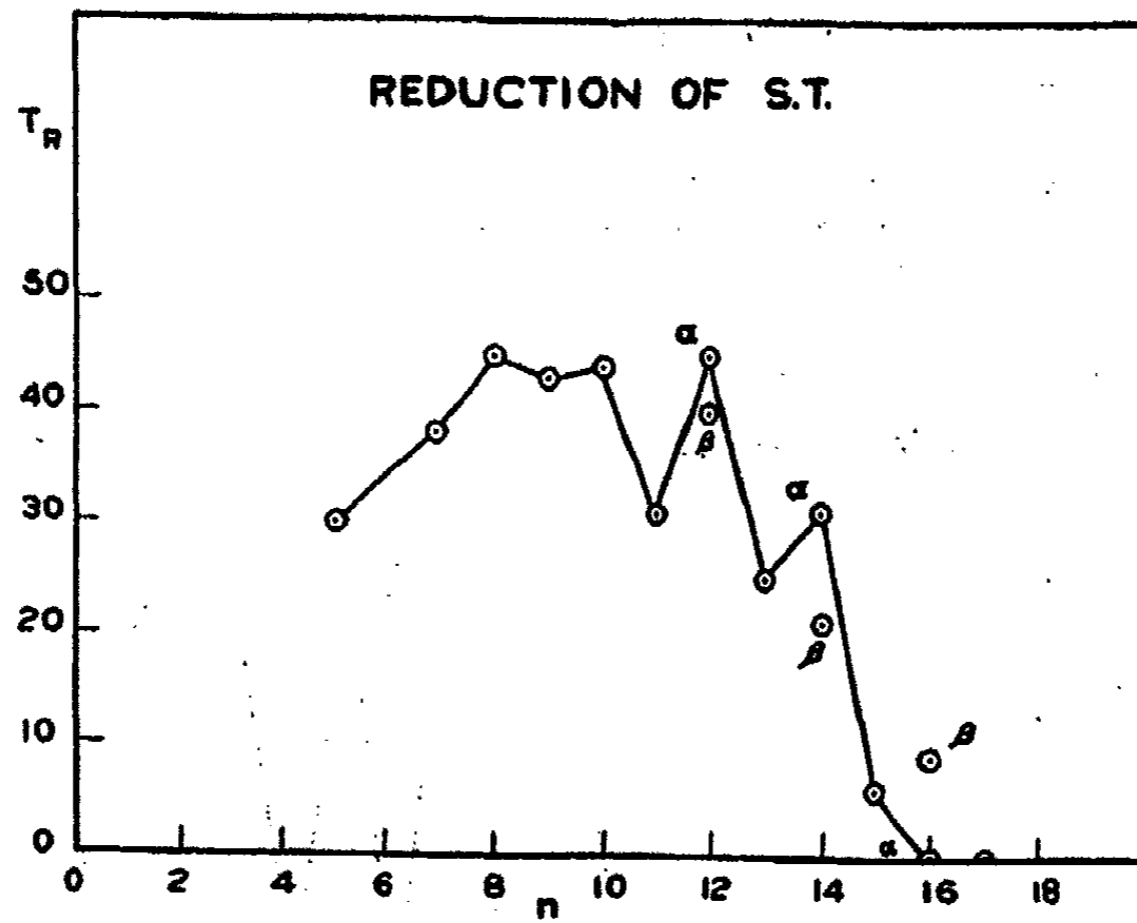


FIG. 3

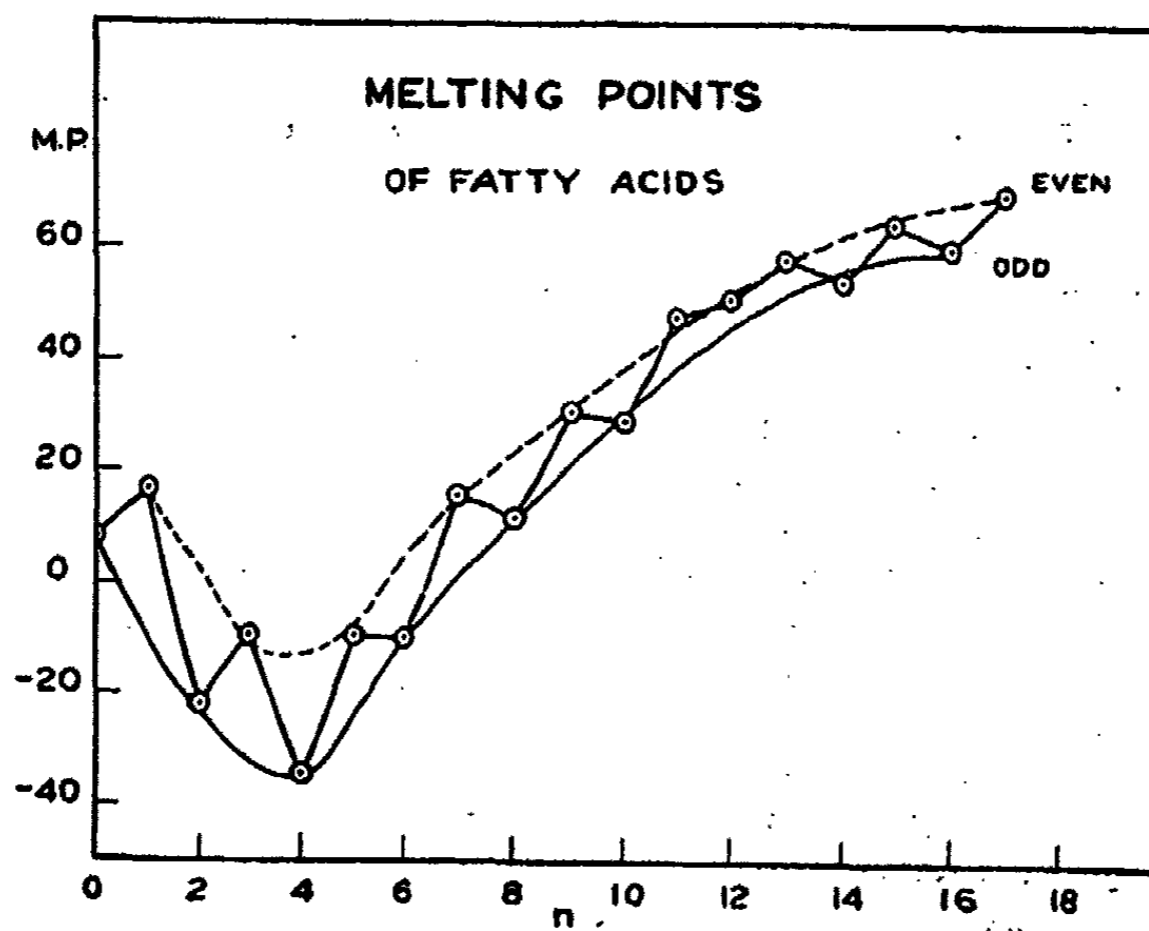


FIG. 4

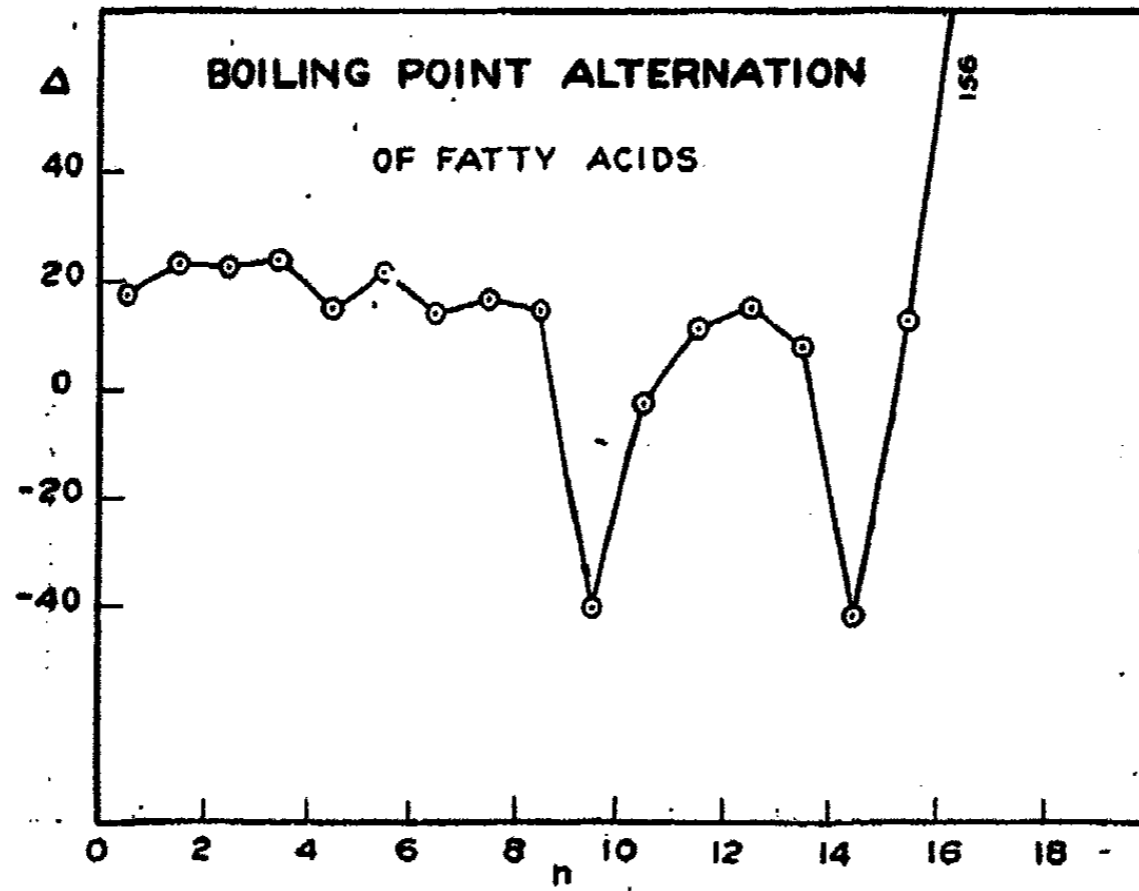


Fig. 5

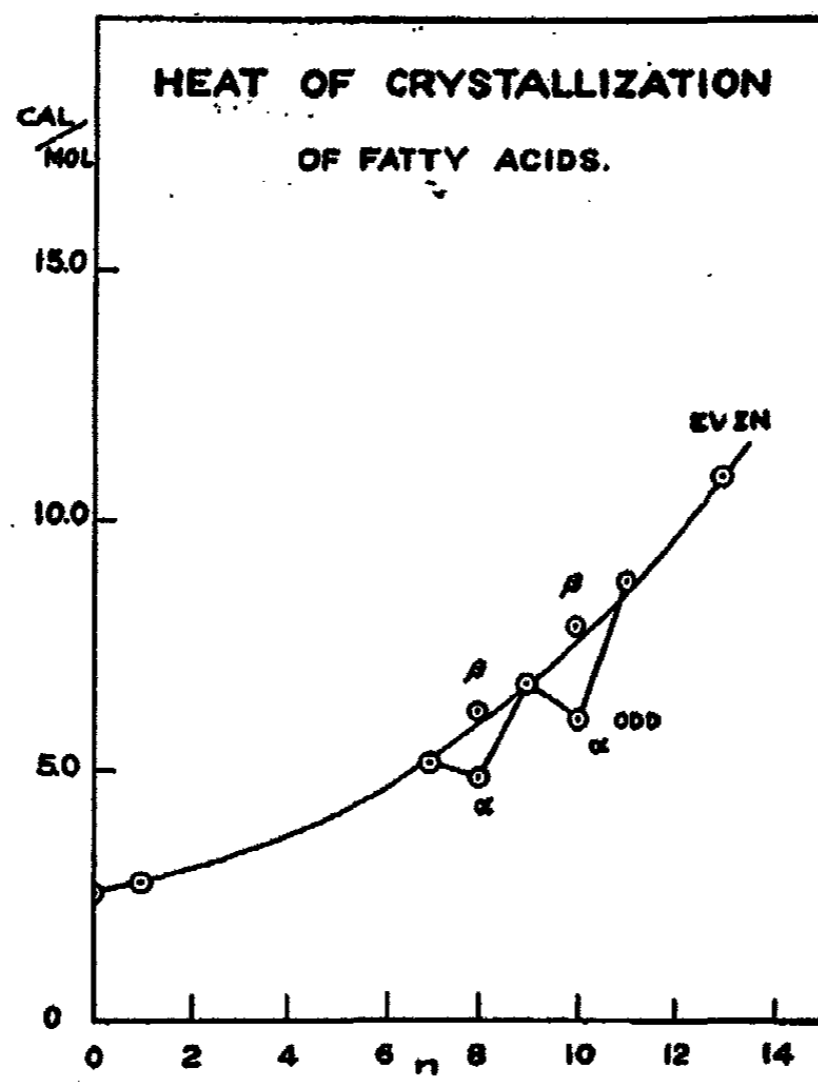


Fig. 6

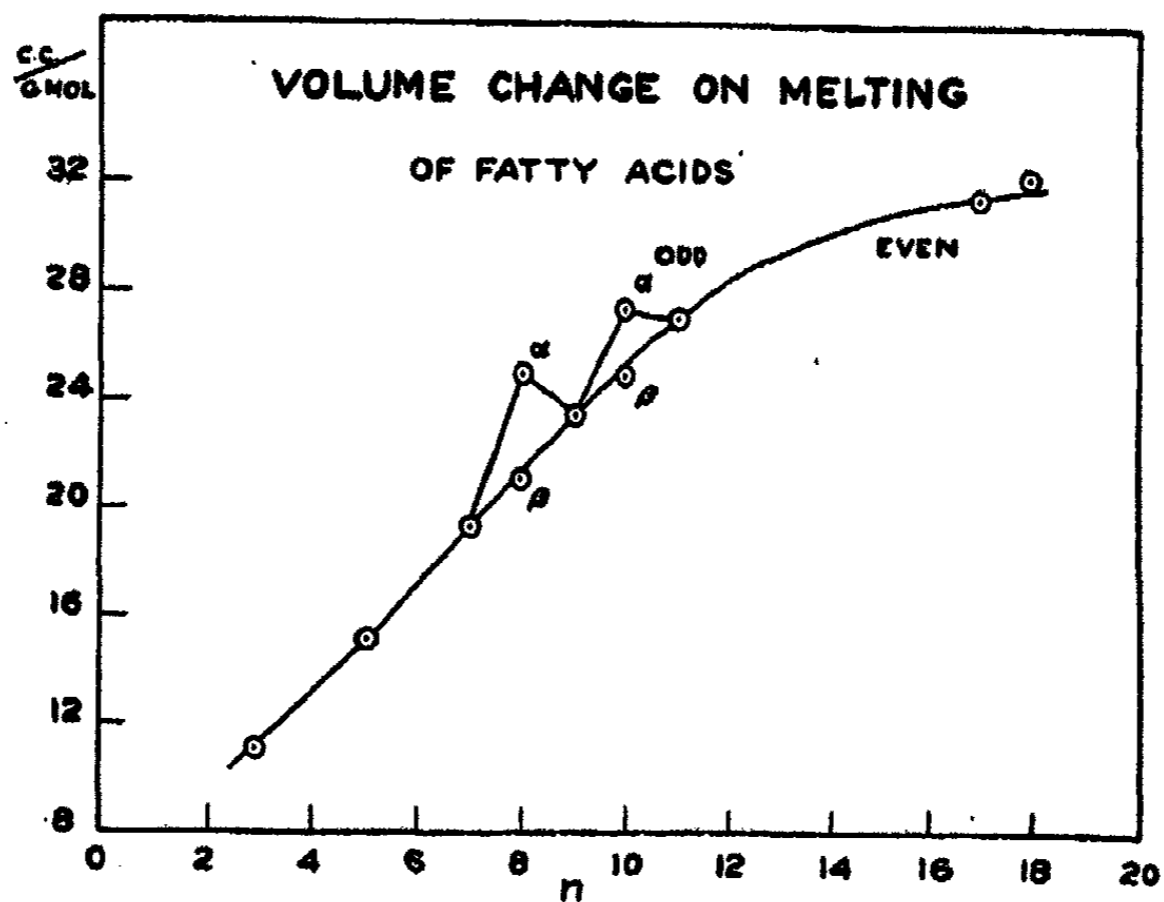


FIG. 7

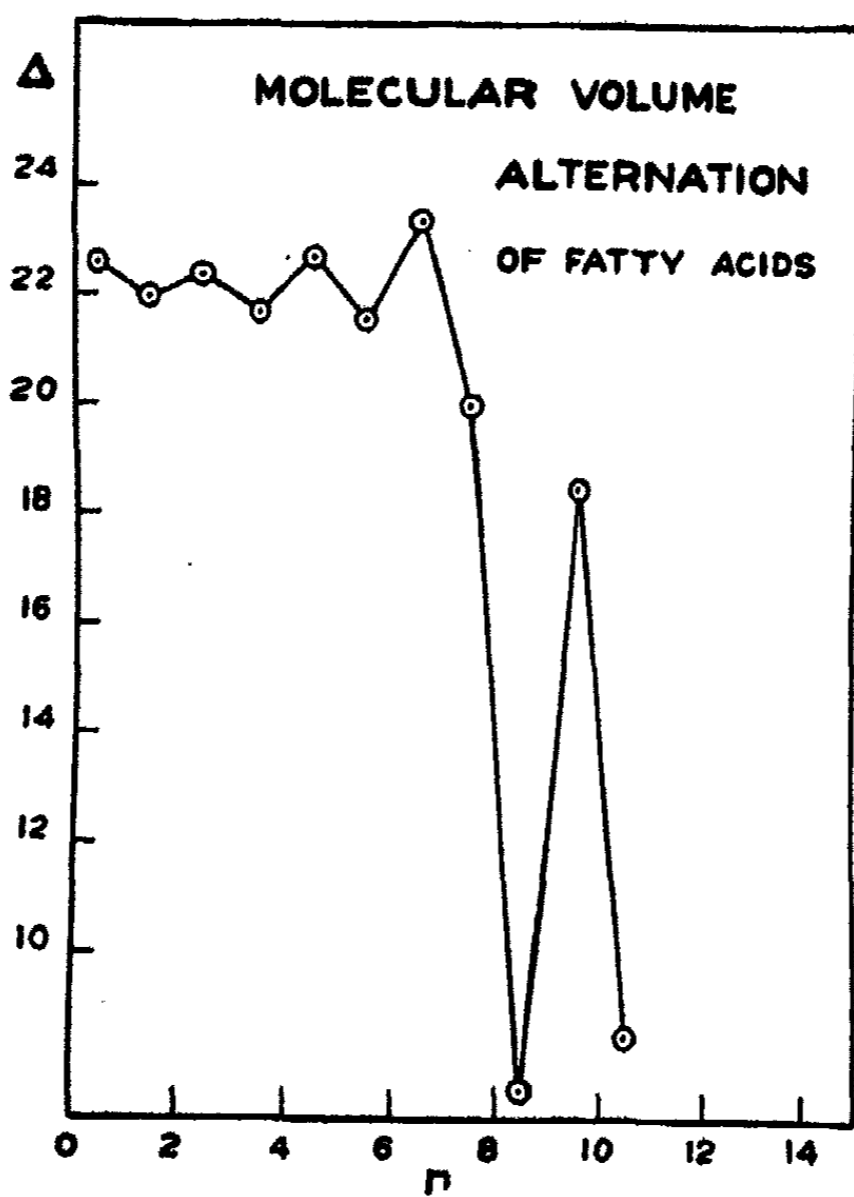


FIG. 8

data on other physical properties of the saturated fatty acids. Most of these show the alternating effect quite clearly. Fig. 9 is of particular interest. It is taken from a recent paper by Smith and Boone on "The Alternating Behavior of Fatty Acids added to Rubber Compounds."¹ The curve shown for

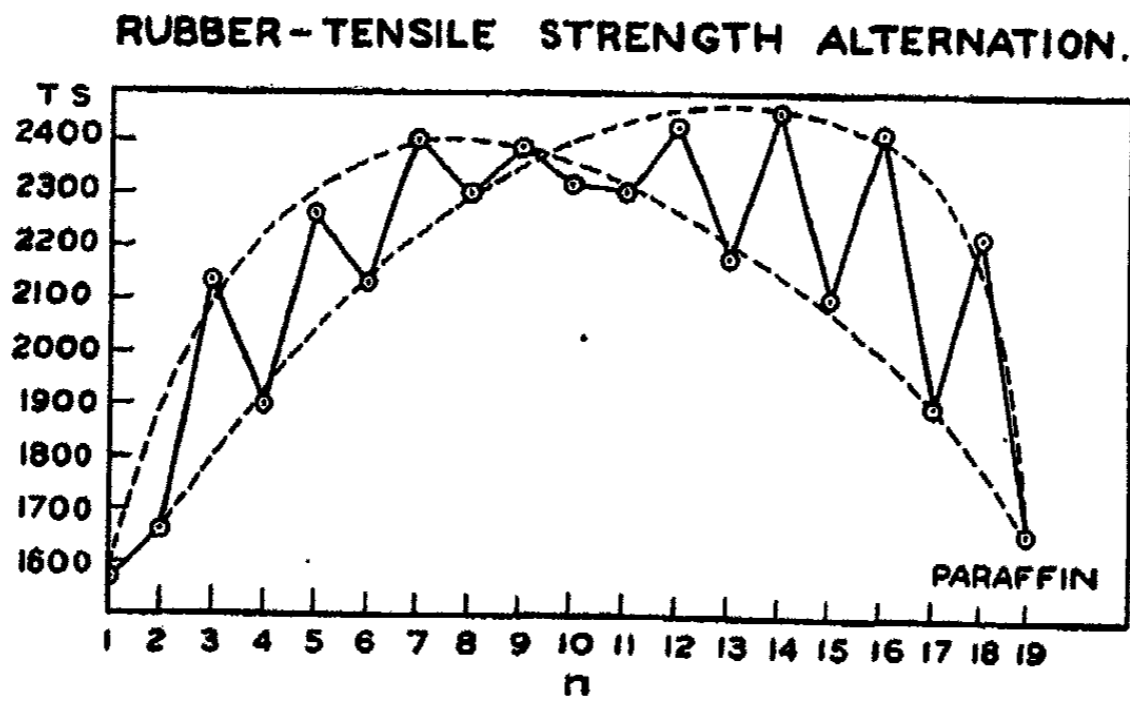


Fig. 9

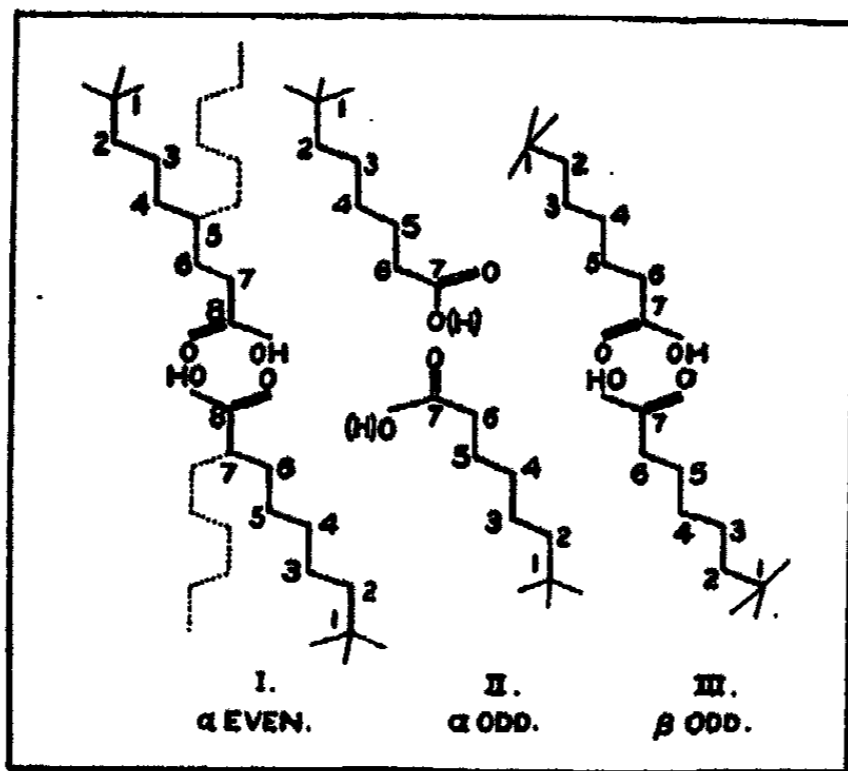


FIG 10.

the tensile strength of rubber against the number of carbon atoms of the acids added (1/15 mol. per 100 gms. of rubber) represents the only data so far discovered which seem to bear any relation to the results of the present work on adhesion of the fatty acids. In Fig. 9 the odd acids have a maximum at about 7 carbon atoms and the even acids at about 14. The general average maximum is in the neighborhood of 11 carbon atoms. The phenomena ex-

¹ Ind. Eng. Chem., 19, 398 (1927).

hibited in Fig. 9 are undoubtedly related in some way to work of adhesion shown in Fig. 1. It should eventually be possible to correlate these properties.

The explanation adopted for the alternation exhibited by the odd and even acids is that first suggested by Garner and Randall in a recent paper on the "Heats of Crystallization."¹ They attribute the difference between an even acid and the next higher odd acid to a change in the crystal structure. The x-ray crystal structure suggested for these various acids is shown in diagram in Fig 10, in which I is the structure of the even acids, II that of the α

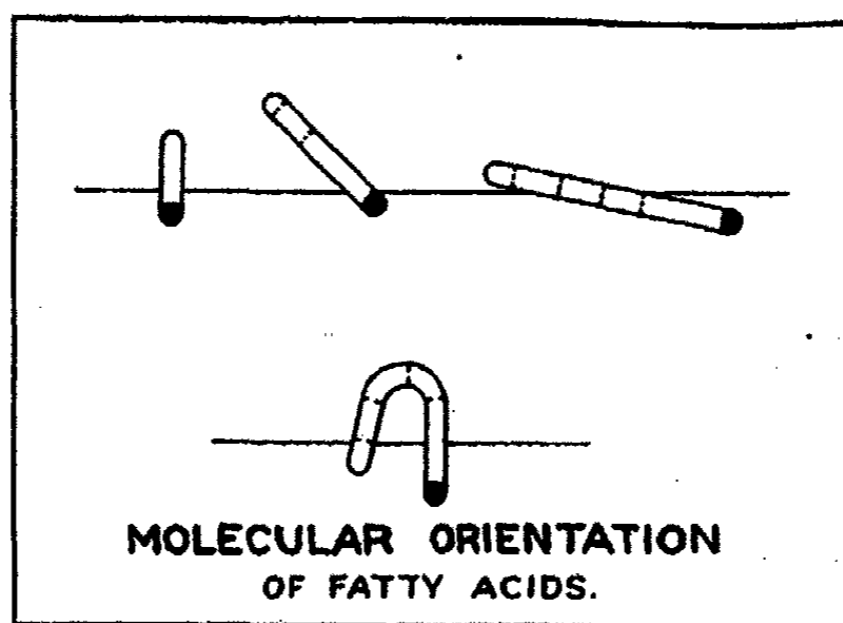


FIG. 11

odd acids, and III the β odd acids. The type of structure represented by I has been thoroughly studied and verified by the work of Bragg and Müller and Shearer and others, also agreeing with results of Langmuir on the dimensions of the molecule. The crystallized acids consist of parallel chains of carbon atoms, the unit cell consisting of two molecules placed end to end with their carboxyl groups adjoining. The angle between two adjacent carbon atoms has been definitely shown to be about 109° or the same as the angle between carbon atoms in the diamond. This permits of the pattern indicated either by the full line or the dotted line. In I and III Garner and Randall assume that the carboxyl groups face each other as shown, in each case a hydroxyl group facing an oxygen. In case II the hydroxyl and oxygen groups are staggered, one oxygen on one side, and one hydroxyl on the other being left relatively free. Consequently, we should expect that in cases I and III the residual valences of the oxygen and hydroxyl groups would be rather completely satisfied. In case II we might expect the hydroxyl group on one side and the oxygen on the other to possess definite stray fields of force or residual valence. On this basis I and III should give results for work of adhesion which fit in together whereas the α odd acids as shown by case II, should show markedly higher values for work of adhesion. This prediction is ful-

¹ J. Chem. Soc., 125, 881 (1924).

filled by the results of Fig. 1. It is therefore felt that the hypothesis of Garner and Randall is well supported by these measurements and their explanation of the cause of the alternation is adopted.

The alternation has therefore seemed to be capable of elucidation. The general trend of the results, however, with a definite minimum in the neighborhood of 13 carbon atoms for the even acids and 12 carbon atoms for the α odd acids, and in particular the marked increase in work of adhesion for the higher acids, is entirely unexpected and difficult to account for. The first part of the curve (Fig. 1) from six to thirteen carbon atoms is in accord with

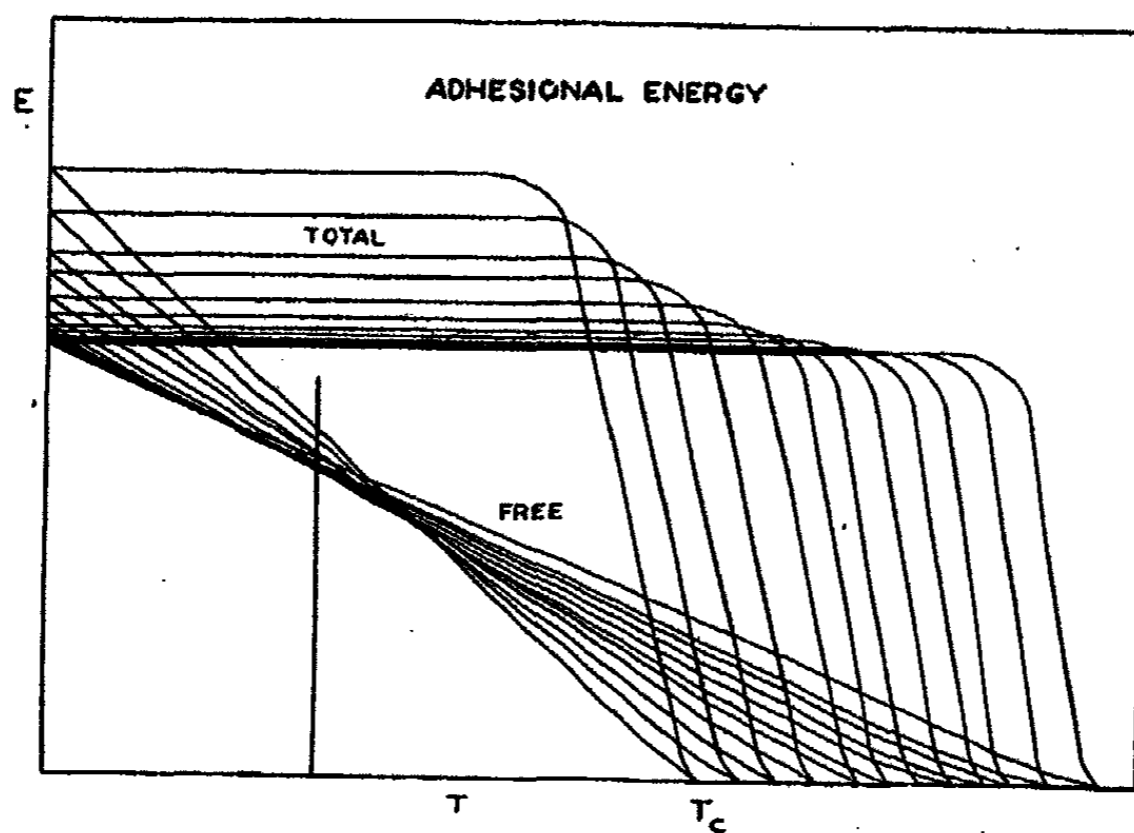


FIG. 12

what we should expect, it being assumed that an indefinite increase in the length of the inactive portion of the chain would result in fewer molecules being perfectly oriented with carboxyl groups towards the water. This is illustrated in Fig. 11 where the molecules and the carboxyl groups at their ends are shown in a conventional manner. When the molecules are short and have a certain amount of mobility, it is relatively easy for a large number of them to turn their carboxyl groups toward the water. As they increase in length a certain number of them would be likely to lie at such angles that others are prevented from turning their carboxyl groups toward the water. Others may bend over as shown by the lower figure, producing the same effect. The net result is that a smaller number of carboxyl groups come in contact with water and there is consequently lower work of adhesion. This crude mechanical explanation immediately falls down after we pass the minimum point.

A hypothesis of a purely speculative nature has been suggested to the writer by Dr. E. K. Carver. Use has been made of the energy-temperature relation in an attempt to construct a picture satisfying the requirements. A diagram for total adhesional energy and free adhesional energy against

temperature can be drawn in a manner exactly analogous to the relations for total surface energy and free surface energy. Harkins and his collaborators have shown that, like total surface energy of a liquid, the total adhesional energy, over a certain range, is independent of the temperature, probably in a manner similar to the former. They have further shown that the free adhesional energy or work of adhesion varies with the temperature very similarly to the free surface energy or surface tension of a liquid. It therefore seems quite correct to construct the diagram as indicated.

Unfortunately, any data which might be of help in establishing or refuting this hypothesis, are lacking. The precision of contact angle measurements

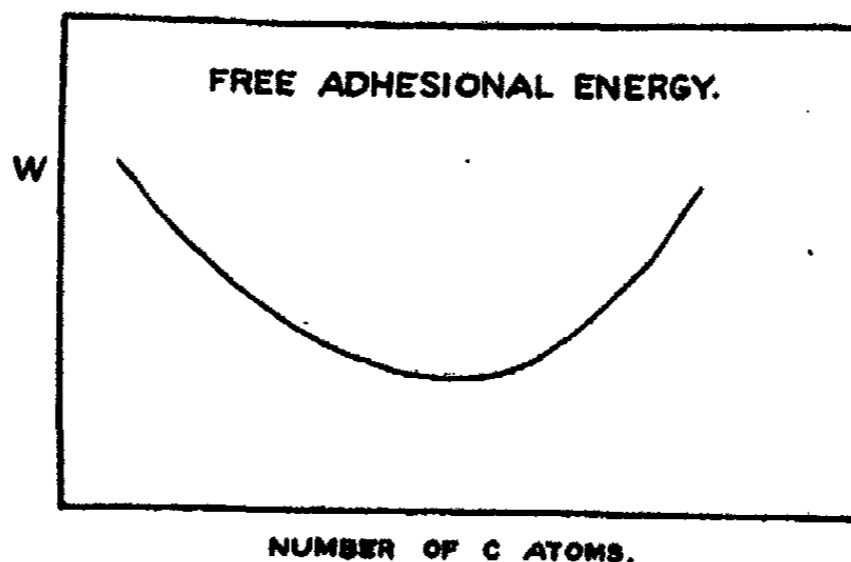


FIG. 13

is not yet great enough to allow the measurement of the temperature coefficient of the adhesional work. This has been done by Harkins for a number of liquids but the measurement of liquid interfacial tensions can be made many times more precise than can the results for contact angles of solids, where many uncertain factors are involved. Consequently, we are unable to indicate from experimental data the exact nature of the energy-temperature relation. Fig. 12 represents a family of curves drawn entirely on an arbitrary basis and representing really only a pure guess as to possible relations. The upper set of curves represents the total adhesional energy for successive or regularly increasing homologues. The other set of curves joining the extreme ends of the first set shows the relations for the free adhesional energy. If we now take a cross-section of the latter set of curves at the point shown by the vertical line, the values of the free adhesional energy or work of adhesion show a relation with the number of carbon atoms indicated in Fig. 13. This is a curve having a minimum point bearing some resemblance to the results shown in Fig. 1.

This hypothesis has not as yet been fully developed and admittedly lacks experimental evidence. It would seem also to be scarcely sufficient to explain alone the general trend of the results for the fatty acids. Nevertheless, it is

felt that the explanation just suggested is at least in part correct and is partially responsible for the great change in work of adhesion with number of carbon atoms.

It is believed that the effect of the length of the chain must in some part be responsible for the results obtained. The short chain acids are more polar than the long chain acids—that is, the carboxyl group seems to possess a stronger residual valence when attached to relatively few methylene groups. The short chain acids, for example, possess higher solubility and are much more strongly acid. For purely mechanical reasons, these short molecules are also able to orient themselves with much greater ease. A large number therefore will be oriented with their carboxyl groups in the same direction.

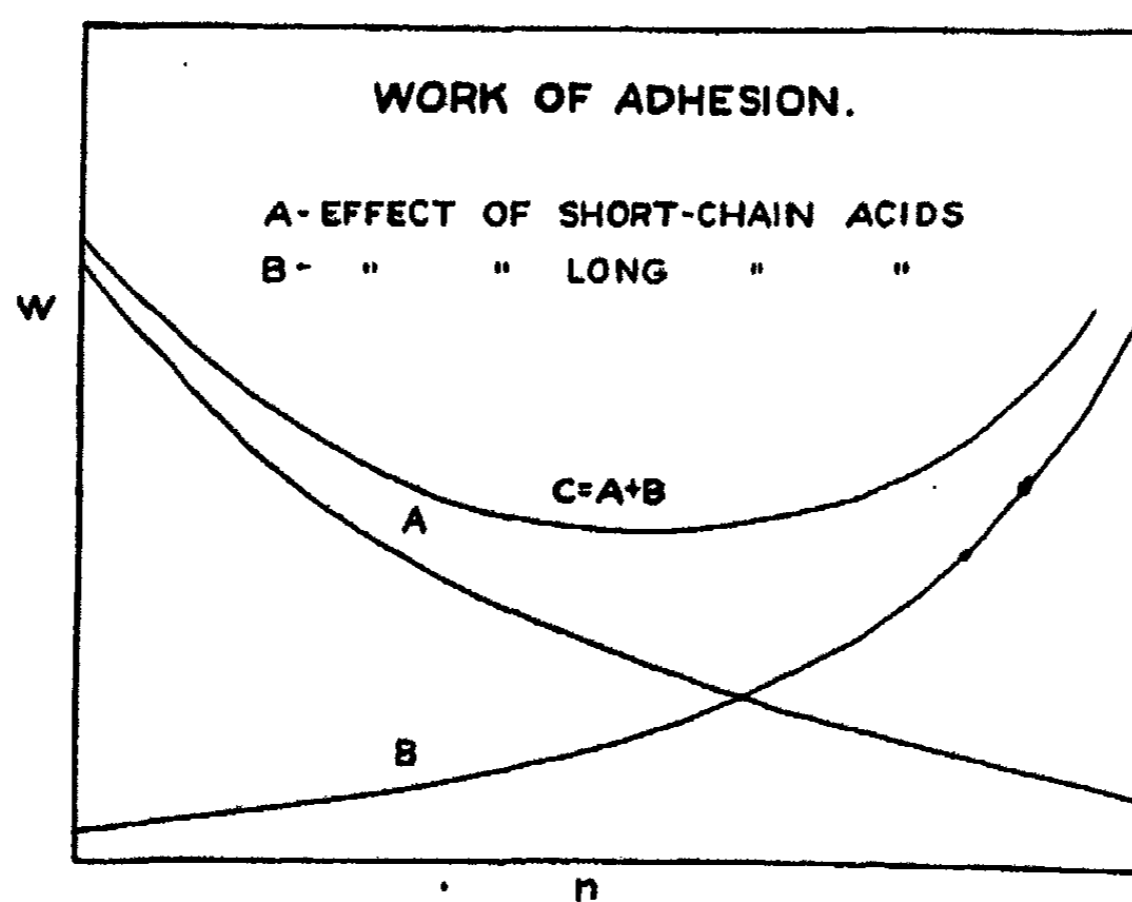


FIG. 14

As the length of the chain increases, the ease of orientation decreases and the consequent effect on the work of adhesion may be roughly indicated by Curve A, Fig. 14.

At the same time as the chains increase in length there are two effects which will tend to keep the molecules in place once they are oriented. The first of these is the mechanical effect of the long chain making it more difficult for the molecule to move about or turn and the second is the mutual attraction of the methylene groups for each other producing the same result. Consequently, as the number of carbon atoms increase we shall have a gradual increase in the number of molecules which are oriented and remain so, and this effect may be represented by Curve B, Fig. 14. The net result of the two effects shown by Curves A and B will be a curve of the shape shown in Curve C. It is seen that Curve C, Fig. 14, and the curve of Fig. 13, are both

in the direction of the general results for work of adhesion shown in Fig. 1. It is therefore believed that both effects are jointly responsible for the shape of the latter curve.

Summary

1. When work of adhesion of the fatty acids is plotted against number of carbon atoms, the adhesional work shows a marked minimum in the neighborhood of 12 to 14 carbon atoms, beyond which there is a very pronounced increase.
2. The alternating effect shown by odd and even acids is very marked, the odd acids showing two enantiotropic forms. The β odd and even acids lie on a single smooth curve, the α odd modifications showing alternating higher values.
3. The alternation and two sets of values for α and β odd acids are attributed to differences in crystal structure. (See Fig. 10)
4. The general trend of the curve for adhesional work against number of carbon atoms is considered as partly due to the general nature of the adhesional energy-temperature relations and partly to the mechanical effects of the length of the carbon chain.

CATALYTIC REDUCTION OF NITRO-ORGANIC COMPOUNDS IN THE LIQUID SYSTEM

BY O. W. BROWN, G. ETZEL AND C. O. HENKE

631

Introduction

In this investigation a study of the catalytic reduction of nitro-compounds in the liquid phase was undertaken. The compounds reduced were: nitrobenzene, α -nitronaphthalene, p-nitrotoluene, o-nitrophenol, p-nitrophenol and di-nitro toluene. The reductions were carried out with a nickel catalyst, in a hydrogen atmosphere under a pressure of 200 to 700 pounds per square

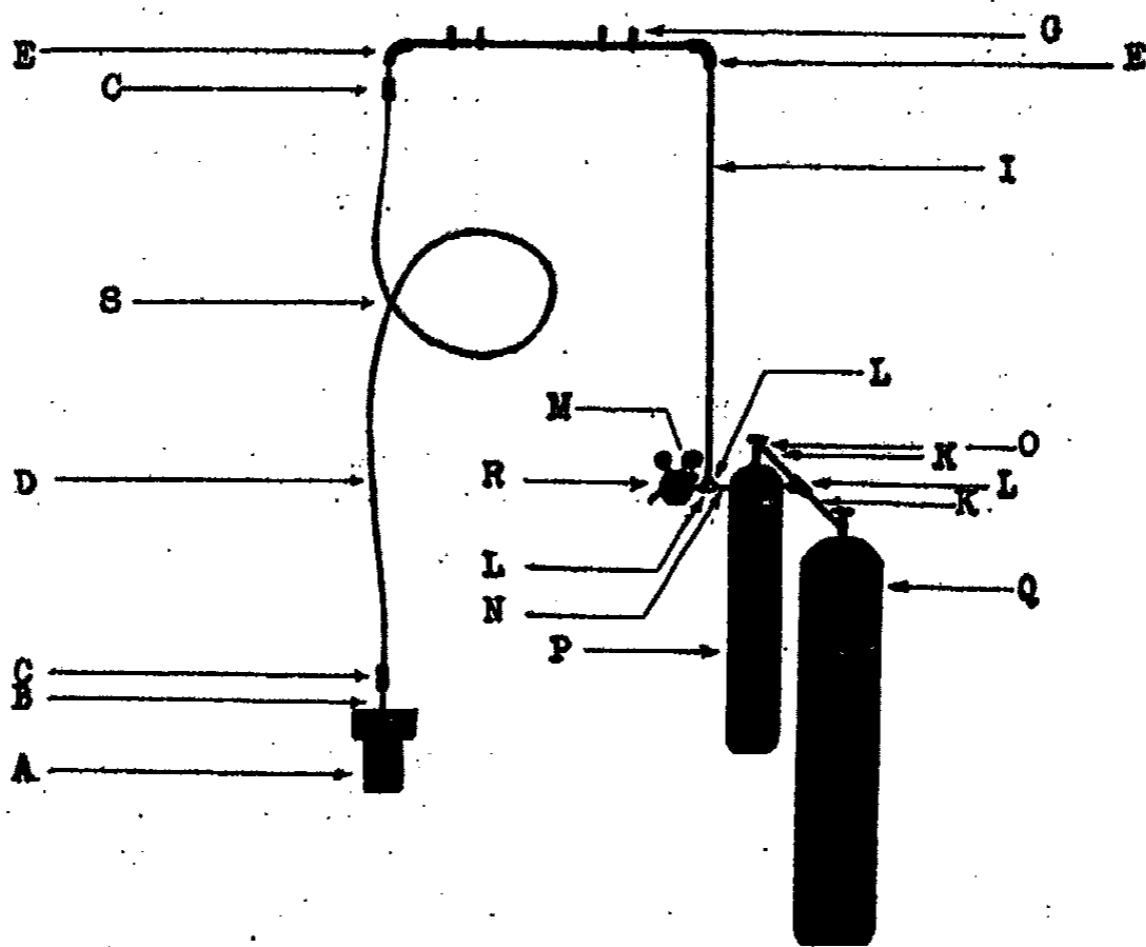


FIG. 1

- A—Autoclave proper, capacity 80 cc., tested for 3000 lbs. per sq. in.
- B—Six in. piece $\frac{1}{2}$ in. rigid hydraulic iron pipe.
- C—Union.
- D—Eight ft. piece $\frac{1}{2}$ in. flexible copper hydraulic pipe.
- E—One-half in. elbow.
- G—Support to attach apparatus to the ceiling of the room.
- H—One-fourth in. steel wire.
- I—Four ft. piece $\frac{1}{2}$ in. hydraulic iron pipe.
- L—"T"
- M—One-half in. nipple 3 in. long.
- N—One-half in. nipple one foot long.
- K—One-half in. hydraulic iron pipe one ft. long.
- O—One-half in. adaptor carrying left-handed female threads.
- P—Small hydrogen tank 4 in. in diameter and 25 in. in height.
- Q—Hydrogen tank, 200 cu. ft. capacity.
- R—Hydrogen pressure gauge.

inch ($15\frac{1}{2}$ to $47\frac{1}{2}$ atmospheres). In order to insure intimate contact between hydrogen, catalyst, and nitro compound, the mixture was agitated

vigorously by shaking. The variable factors studied were: temperature, pressure, amount of catalyst, time of reduction and kind of solvent used.

Brochet¹ states that he has carried out the reduction of some nitro-organic compounds in the liquid phase with a nickel catalyst. A. N. Parret and A. Lowry² have studied the catalytic reduction of α -nitronaphthalene with hydrogen under pressure in presence of a nickel catalyst.

Apparatus

The apparatus used in this investigation was designed by O. W. Brown and C. O. Henke. Fig. 1 shows the apparatus.

The autoclave was shaken by means of an eccentric arm which had a stroke of two in. and was driven by a 1/6 horse power electric motor. Pipe B was threaded to the upper part of the autoclave. The autoclave proper was connected to the autoclave cover by means of six bolts, $\frac{1}{2}$ in. in diameter, S.A.E. threads. The flexible copper pipe D was looped once at S. This loop takes care of the backward and forward movement caused by the eccentric arm. The junction between the cover and the autoclave was sealed by means of a lead gasket.

Heating Element

The heating element consisted of an electric heating jacket. It was made by wrapping asbestos paper around a strong tin can. Then about six turns of No. 18 chromel wire were wrapped around the paper, and the whole covered with more asbestos paper. The ends of the wire were doubled and twisted tightly in order to insure greater strength.

Method of Procedure

Known weights of organic compound and of reduced nickel catalyst were placed in the autoclave, and a definite amount of solvent added. A slow current of hydrogen was passed thru the pipes to wash out all air while the autoclave was being bolted to its cover. The bolts were then tightened and the hydrogen pressure was turned from the large tank until the required pressure was reached. The large tank was then closed. The autoclave was then immersed in water to test for leakage. The purpose of the small tank was to act as a reservoir and to insure an uniform pressure during the reduction period.

The heating jacket was placed in position around the autoclave and connected to a source of current (110 volt).

The temperature of the reaction mixture was determined by means of a thermocouple which was inserted into a hole drilled into the wall of the autoclave. This hole was a $\frac{1}{4}$ in. in diameter bore from one side to the center of the bottom of autoclave. The point at which the temperature was taken was $\frac{3}{8}$ in. above the outer bottom surface of the autoclave and about one in. below the reacting chamber. An iron collar was used to hook the eccentric

¹ Brochet: Bull., (4) 13, 197 (1913); 15, 554 (1914).

² A. N. Parret and A. Lowry: J. Am. Chem. Soc., 48, 778-782 (1926).

arm to the autoclave. A hole was left in the heating jacket for the insertion of the eccentric arm. The temperature required was obtained by adjusting an external resistance.

When the desired temperature was reached the motor was started and the apparatus shaken for a definite period of time, usually two hours, at 150 R.P.M. At the end of this time the heating jacket was removed, the small tank closed, and the autoclave cooled by surrounding with cold water. The hydrogen pressure in the autoclave was allowed to escape thru the gauge.

The autoclave was then opened, the contents examined as to color and odor. It was poured into a two-liter beaker containing 50 cc. of concentrated hydrochloric acid. The autoclave and the lower end of the pipes were carefully washed with alcohol. The hydrochloric acid solution was diluted to two liters, mixed, and portions titrated against a standard solution of sodium nitrite.

Preparation of Catalyst

The nickel catalyst was prepared by igniting the nitrate and then reducing the oxide in hydrogen. The nitrate, with a small addition of nitric acid was ignited in a small porcelain evaporating dish in an electrically heated muffle. The temperature of ignition was measured by a copper constantan thermocouple, the junction being in the dish just above the nickel oxide. The nickel oxide, after cooling, was powdered and put in the furnace as described by Brown and Henke.¹

The temperature of ignition of the nitrate was 560°C. The oxide was reduced at a temperature of 378°C with the rate of flow of hydrogen 14 liters per hour.

Material Used

Nitrobenzene used was purified by shaking it with sodium carbonate solution and then steam-distilling it. The distillate was dried with calcium chloride and then redistilled twice. The hydrogen used for reduction was commercial hydrogen. The α -nitronaphthalene used was a C.P. product from Eastman Kodak Co.

Experimental Part

A series of experiments was first made to ascertain the best temperature and pressure. The amount of nitrobenzene used in each experiment was 4.7354 g. The amount of benzol, which was used as a solvent, was 8 cc. Results obtained are given in Table I.

TABLE I

| Amount of reduced nickel catalyst | | | 2.5 g. | | |
|-----------------------------------|------------------------------|----------------------|------------------|------------------------------|----------------------|
| Time of reaction | | | 2 hrs. | | |
| Temperature C | Pressure lbs. per sq. in. | Amine % of theory | Temperature C | Pressure lbs. per sq. in. | Amine % of theory |
| 190 | 500 | 99.05 | 215 | 200 | 25.04 |
| 215 | 500 | 100.03 | 215 | 300 | 67.45 |
| 253 | 500 | 95.54 | 215 | 500 | 100.03 |
| 282 | 500 | 52.53 | 215 | 700 | 100. |

¹ Brown and Henke: *J. Phys. Chem.*, 26, 161-190 (1922).

The experiments of Table I indicate that 215°C is the best temperature for the reduction when a pressure of 500 lbs. is used. By changing the temperature 20°C above or below 215°C the yields vary slightly, while by a constant increase they suddenly drop. By varying the pressure and keeping the other factors constant we notice that as the pressure increases the yields increase, 500 lbs. per sq. in. giving a quantitative reduction.

Table II gives the results of a study of the variation of the amount of catalyst and time of reaction.

| Amount of Catalyst g. | Temperature Pressure Solvent Benzol | Time of Reaction minutes | 215°C 500 lbs. 8 cc. | Amine % of theory |
|--------------------------|-------------------------------------------|-----------------------------|----------------------------|----------------------|
| 2.5 | | 15 | | 3.96 |
| 2.5 | | 30 | | 93.21 |
| 2.5 | | 60 | | 99.21 |
| 2.5 | | 120 | | 100.3 |
| 1. | | 120 | | 43.42 |
| .1 | | 120 | | 16.06 |

Experiments described in Table II show that the maximum yields were obtained when the reaction was allowed to take place for the period of two hours, although a good yield was obtained when the period was one hour. Two and one half grams of catalyst for 4.7354 g. of nitrobenzene gave the best results. The yields decreased quite rapidly with a decrease in the amount of catalyst.

Effects of different solvents on reduction of nitrobenzene were tried. The results are shown in Table III.

| Solvent Used | Amount of Solvent cc. | Temperature Pressure Amount of Catalyst Time of Reaction | 215° C 500 lbs. 2.5 g. 2 hrs. | Amine % of theory |
|------------------|--------------------------|-------------------------------------------------------------------|----------------------------------------|----------------------|
| None | — | | | 99.94 |
| Benzol | 8 | | | 100.03 |
| Absolute Alcohol | 8 | | | 99.78 |

It is seen from Table III that quantitative yields were obtained with or without solvent.

A few experiments were carried out on the reduction of α -nitronaphthalene to α -naphthylamine at a pressure of 500 lbs. A. N. Parret and A. Lowy¹ reduced this same compound using a pressure of 50 to 100 lbs. and ob-

¹ A. N. Parret and A. Lowy: J. Am. Chem. Soc., 48, 778-782 (1926).

tained with nickel catalyst a maximum yield of 70%. The results obtained by the writers are given in Table IV.

TABLE IV

| | | |
|--------------------------------------|--------------------------|----------------------|
| Temperature | | 215°C |
| Pressure | | 500 lbs. |
| Amount of catalyst | | 2.5 g. |
| Amount of α -nitronaphthalene | | 4 g. |
| Time of reaction | | 2 hrs. |
| Solvent | Amount of Solvent cc. | Amine % of Theory |
| Benzol | 8 | 99.55 |
| Ethylene Glycol | 10 | 89.78 |
| Ethyl Alcohol | 10 | 98.31 |

Better yields were obtained with benzol as solvent than with either ethyl alcohol or glycol. The latter was the poorest. Brown, Henke and O. C. Criswell reduced in this laboratory *p*-nitrotoluene, with a pressure of 500 lbs. per sq. in. and 215°C. A quantitative reduction was obtained. *O*-nitrophenol, *p*-nitrophenol and di-nitrotoluene were also quantitatively reduced. The conditions were as follows: temperature 226°C, pressure 500 lbs. per sq. in., solvent used absolute alcohol, catalyst nickel made by reducing nickel carbonate at 378°C.

Conclusions

1. Experiments were conducted showing that liquid nitrocompounds and nitrocompounds in suitable solvents can be reduced quantitatively to amines, with hydrogen under pressure, and with a nickel catalyst.
2. Quantitative reduction of nitrobenzene, α -nitronaphthalene, *p*-nitrotoluene, *o*-nitrophenol, and di-nitrotoluene was obtained at 215°C and at a pressure of 500 lbs. per sq. in.
3. For the best results 0.52 g. of nickel catalyst was required for each gram of nitrocompound reduced.
4. Benzol and ethyl alcohol were solvents that permitted quantitative reduction of nitrocompounds studied.

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NEW BOOKS

Pyrometry. By *W. P. Wood and J. M. Cork.* 23 × 16 cm; pp. viii + 207. New York and London: McGraw-Hill Book Company, 1927. Price \$3.00. In the preface the authors say, p. v.: "while there are a few reference books on pyrometry there is no work which is organized in such a manner as to be of great utility as a textbook for college students. Instructors have been forced to handle the subject entirely by lecture or by personally prepared sets of notes. This manuscript, therefore, has been assembled with the needs in mind of the student as well as of the man more experienced in the uses and the theory of pyrometry. Questions and problems are added at the end of some of the chapters. Outlines for laboratory experiments are included. These are largely suggestive and may be modified to meet local conditions."

The headings of the chapters are: temperature scales; fluid thermometers; thermoelectric pyrometers; resistance thermometers, optical pyrometers; total radiation pyrometers; temperature recorders and controlling devices; transition points and thermal analysis; refractory materials used in pyrometry.

"Most gases obey Boyle's law very closely at temperatures distant from their condensation points. When used for temperatures close to the condensation point, the error in the normal thermometer is surprisingly small. Kammerlingh Onnes tested this effect by comparing a hydrogen thermometer with a helium thermometer at temperatures close to the condensation point of hydrogen and found that the error was negligible when distant from the condensation point by 0.5°. . . . The hydrogen thermometer deviates 0.005° from the thermodynamic scale at -100° and 0.004° at +1000°," p. 13.

"The fact that the gas scale is fundamental by agreement should not be overlooked, however, and since it has not been used above 1550°C., higher temperatures can only be measured by extrapolating certain laws which have been found to hold true below this value. Hence for these higher temperatures, an element of uncertainty exists and it is only by extrapolating with several different laws, which have been independently verified in the known region, and by obtaining in each case the same value at the higher temperature that confidence is placed in the result. The uncertainty attendant upon extrapolations of this sort is well illustrated by the following early experiment in high-temperature measurement carried out by Wedgwood. He attempted to measure temperature by the shrinkage caused by that temperature upon a certain sample of clay. The measuring of the shrinkage for the known temperature interval from the freezing to the boiling point of water sufficed for a calibration of the instrument. By comparing this shrinkage with that which took place when the clay was placed in a furnace at the temperature of melting iron, he expressed the melting point of iron as about 12000° C., a value about 10500° too large," p. 16.

"The length of the couple which lies within the heated zone is of great importance. This is sometimes called the "depth of immersion." If a couple is insufficiently immersed, conduction to the outer, cooler sections is so high that the reading of the couple will be low. It is a good practice to insert the couple just as far as possible. This will insure satisfactory results as a rule, but in cases where it is suspected that the immersion is not sufficient, the temperatures along the protecting tube should be explored and if there is a sudden drop near the hot end of the couple, means should be taken to produce a sufficient immersion.

"Some couples are purposely immersed an insufficient distance. This is done when the temperature of the furnace is so high that there is danger of fusing the couple and tube. Although the temperature read is low, it is possible, by correlation with physical changes of material within the furnace, to obtain a fairly accurate idea of the temperature for future operations," p. 60.

"The assumptions made in the development of Planck's formula led to the now famous quantum theory. Many precise experiments have been made to test the validity of this

equation and the conclusion seems to be that it fits the experimental facts very closely throughout the entire wave-length range for the temperatures used in the experiments, which have been from 400 to about 1500°C," p. 85.

"In an optical pyrometer, brightness match is obtained between the filament and the image formed by the objective, regardless of the history of the radiation before coming to the objective. The radiation might, therefore, come from a reflecting surface which is itself cold. The apparent temperature of the body would in this case be much greater than its true temperature. For example, a wall in sunlight might have an apparent temperature of 2000°C. Hence, care must be taken that the body whose temperature is being determined is not reflecting radiation from another bright source," p. 104.

"In a progress report on optical pyrometry recently published, many of the following remarks are included: optical pyrometry has grown to mean almost exclusively high-temperature measurements with the disappearing-filament type of pyrometer. This type is simple in construction, affords great accuracy and is adapted to a diversity of conditions. While the optical pyrometer may still be regarded as a secondary device, so much experimental confirmation of the quantum theory and consistent experimental values of the radiation constants have been obtained that it seems reasonable to make use of it in checking the high-temperature gas scale. The precision, accuracy and wide range of usefulness of the disappearing-filament optical pyrometer depend on perfect disappearance of the filament with high resolving power and magnification by the eyepiece. By designing the instrument to avoid diffraction effects, Fairchild and Hoover state that it is possible to obtain a precision of 0.2°C. or better at the melting point of gold. To test the consistency of the high temperature scales in use in various research laboratories in this country and England, Forsythe recently compared the current-temperature relations for certain lamps found in these various laboratories. These high-temperature scales are based upon assumptions regarding the melting point of a metal and a value of the c_2 radiation constant. Thus the basis of the scale at the General Electric Research Laboratory and the U. S. Bureau of Standards is $c_2 = 14,350$ and the melting point of gold, 1063°C. At the National Physical Laboratory, England, $c_2 = 14,350$ and the melting point of palladium, 1555°C. The agreement of the scales was found to be very good, differences being only a few degrees over the range from 1000 to 2400°C.," p. 108.

"An objection to an instrument of the total-radiation type arises from the fact that the objective lens, if made of glass, absorbs a large part of the radiation incident upon it, especially in the infra-red spectral region. Since most of the radiant energy from bodies at temperatures not exceedingly high lies in the infra-red region, the sensitivity of the apparatus is greatly reduced. Further, the fourth-power law or any other simple expression does not apply to the radiation transmitted by the glass lenses. Fluorite (calcium fluoride) has a remarkably small and almost constant absorption coefficient for all wave-lengths up to 10 μ , and would be a suitable material from which to make the lenses of the instrument. Its use, however, is limited by its expense. To overcome this objection Féry in 1904 suggested the use of a concave mirror similar to the astronomical reflector to replace the lenses," p. 116.

Wilder D. Bancroft

The Electronic Theory of Valency. By Nevil V. Sidgwick. 24 X 16 cm; pp. xii + 310. London and New York: Oxford University Press, 1927. Price: 15 shillings; \$5.00. This book is uniform with the recent books in the same series by Hinshelwood and by Paneth and Hevesy; it is excellently produced, but is still sufficiently expensive in this country to make it worth while to place one's order in England.

In the case of the compounds of one of his elements, carbon, the chemist has, in part at least, succeeded in bringing order out of chaos, and the resulting system is the realm of organic chemistry. In the realm of inorganic chemistry, however, the chemist is still oppressed by a heterogeneous collection of disorderly facts. The timely and very welcome volume before us helps to keep alive the hope that, in the not too distant future, the in-

organic chemist may be able to show that, by a deductive method, his myriad molecules with their properties and reactions are entirely predicable from a knowledge of the relatively small number of chemical atoms that enter into them.

In developing the theory of valency, Professor Sidgwick adopts the concepts of atomic physics, and tries to explain the chemical facts in terms of these; realising however, as certain others have failed to do, that one should not use the terminology of physics unless one is prepared to recognise its laws. Writing today, the author of a book on the *electronic* theory of valency must needs anticipate the criticism that the newer wave mechanics has already dissolved, or at least sadly attenuated, the so-called electron. Professor Sidgwick meets this criticism in his preface, as Sommerfeld, Richardson and others have done before him.

The earlier chapters deal very concisely with atomic structure and lead up to a table of structures compiled with help from Dr. Stoner. "Subgroups" and "grouplets" are here carefully distinguished with reference to the *k* and *j* quantum numbers, because, of necessity, use is later made of these terms,—terms which were unknown when G. N. Lewis's book on valency was published.

As was to be expected, in developing the fundamental principles of valency a very clear presentation is given of what Sidgwick has called the "coordinate link." For the past few years the reviewer has devoted two or three lectures annually to Sugden's parachor. Here for the first time to his knowledge the parachor is discussed in a textbook, and used, of course, in evidence for the coordinating linkage. Using the nomenclature which he suggested at the 1927 meeting of the British Association, Sidgwick distinguishes "donor" from "acceptor" atoms, terms which prove useful in discussing—without diagrams the chelate rings of Morgan, associated liquids and other topics. Another Sidgwickian contribution is dealt with in the chapter on covalency maxima. Does the famous octet still survive? Yes, most certainly, but it is no longer all-important. How do we now explain the substantial fact that carbon and silicon, so closely analogous in their hydrogen and halogen compounds, are so radically unlike in their dioxides? Lewis suggested that silicon, being an element beyond the second period, could not form double bonds; Sidgwick suggests that, by the covalency maximum rule, the maximum covalence of the second period element carbon cannot exceed four, whereas a third period element like silicon may have a covalence of six. The concepts of "pure" or "mixed valency groups" and of "effective atomic number" help the author to catalogue and classify the valency groups which, in practice, are found to be stable; and the last named conception helps to make clear the wonderful promise of work like that of Welo and Baudisch on paramagnetism in complexes.

Aside from his own contributions, other people's ideas are very clearly presented in the discussions on solubility, solvation, Werner's theory of coordination, Fajans' valence theory, molecular magnetism, stereochemical relations and chelate rings. It is vastly convenient to have so many relevant modern ideas marshalled together in a well-digested form.

The book closes with a systematic study of the periodic groups in the light of the discussion that has gone before, involving some repetition of this but also some anticipation of the material of a second volume which the author promises and to which everyone who has read this first volume must look forward with pleasure.

The attention of the author will be drawn to any errors or obscurities that have met the observation of the group of over a dozen graduate students with whom the reviewer has gone over the book. These errors and obscurities are few in number. At many points, there is room for difference of opinion; and this is what makes the book stimulating. For example, Sidgwick refuses to go as far as Sugden in the matter of single electron bonds, but he boldly tells us the facts as to bivalent hydrogen, and this is very wholesome for the souls of the conservative.

We owe a debt of gratitude to Professor Sidgwick for this scholarly and inspiring book.

Alan W. C. Mensies

The Theory of Strong Electrolytes. A General Discussion held by the Faraday Society, April, 1927. 24.5 × 15.3 cm; pp. iv + 212. London, 1927. Price: 15s. 6d. The Faraday Society has in the past rendered valuable services to Physical Chemistry, not only by the publication of its *Journal*, which now appears monthly and promises to become ever more useful, but also in the promotion of a series of highly successful general discussions on matters of current interest. The present volume, containing an account of a recent discussion, is in every way worthy of its predecessors. A comparison of its contents with those of the volume containing the discussion on "Electrolytic Dissociation" which appeared in 1919 will show how the subject has advanced since that date. The present volume lacks a general account of the whole discussion, in which the various points of view are co-ordinated and any new ideas or experiments are emphasized. It is to be hoped that future discussions will always be accompanied by such a summary. Much of the material in the volume is in no way new and some of it (especially in the parts dealing with activity) has appeared many times before, so that some little difficulty may be found in ascertaining what is presented for the first time. The volume is divided into two parts, one dealing with the Mobilities of Ions and the other with Activities. In the first part Debye gives a summary of the assumptions underlying his theory, and this is followed by a paper by Onsager in which some corrections which he has introduced into Debye's theory to take account of the Brownian movements of the ions are explained. The new equations give more satisfactory results than the older ones, but they apply only at high dilutions. In moderately concentrated solutions the difficulty as to the precise form which the viscosity correction (which is apparently regarded as necessary) takes was felt by several authors. This is one of the problems awaiting a satisfactory solution.

It is clear from the results quoted in several papers that the initial hypothesis of complete ionisation, which seemed to many to be so well established a year or two ago, will require modification. An "association" of the ions is necessary in many cases even when the concentrations are not high, and there are papers by Fajans, Ferguson and Vogel and MacInnes and Cowperthwaite in which the hypothesis of complete ionisation is attacked on experimental grounds, although the validity of Fajans' arguments was called in question. Onsager points out that in his theory the coefficient of the concentration term may be calculated from the mobilities without any assumptions as to the ionic radii, and it should then be possible to determine the effects of other than electrical forces, for example "association." This is attempted by Hartley and Bell, but these authors have made use of the unmodified Debye formula and their results are, therefore, not free from ambiguity.

A communication from Remy deals with "true" transport numbers (corrected for the transport of water), and there are papers by Ulich and by Hartley and Raikes on mobilities in non-aqueous solvents. Very little new experimental work is brought forward in these papers.

Part Two deals with activity. Much familiar ground is retraversed in this part but the section is enlivened by no fewer than seven experimental papers. Brønsted, Randall, and Harned contribute general articles on the activity of strong electrolytes, including concentrated solutions. Kraus and Seward and King and Partington describe experiments on the influence of one salt on the solubility of another in non-aqueous solutions. Kraus and Seward conclude that the effects are not satisfactorily accounted for on the basis of the Debye theory and that "there are not a few facts that indicate that in solvents of lower dielectric constant it will be necessary to let fall the assumption that the only molecular species present are the simple ions." There are theoretical papers by Bjerrum, Chapman, Fowler, Scatchard, Allmand and Lowry. Bjerrum deals with the interesting problem of heats of solution, which has very recently received attention elsewhere with conflicting results. Allmand and Burrage, Foxton and Shutton and Millet contribute accounts of experiments on the system $KCl-PbCl_2-H_2O$, on the activity of $ZnCl_2$ in concentrated solution (a problem which, it may be mentioned, was one of the first to be dealt with in the study of the thermodynamics of solutions), and on the activity of the hydrogen ion in mixed solvents, respectively. The volume closes with a brief discussion and an index.

Although no new fundamental addition to the theory of strong electrolytes was made during the discussion, the summary of present views, and suggestions as to their probable modification with the advance of experimental knowledge, is useful, and the volume may be recommended as one which most physical chemists will be well advised to possess.

J. R. Partington.

Les Origines de la Chimie colloïdale. By Paul Bary. 20 × 18 cm; pp. 78. Paris: *L'Expansion Scientifique*. Price: 6 francs. The French chemists have rediscovered Baudrimont in a rather interesting way. Some years ago Mr. W. A. Bender, chief chemist of what is now the Certo Corporation, called the reviewer's attention to the fact that Baudrimont had published some very good work on colloid chemistry in 1844-1846, long before Graham. The reviewer published a short note on the subject and the information it contained was apparently as new in France as it was in America.

M. Bary has now published a very welcome biographical sketch of Baudrimont who was a remarkable man in many ways, besides being a man who never missed a fight even if he had to start it himself. According to Baudrimont's own classification he published articles on: the philosophy of science; crystallography, atoms, and the structure of substances; cosmology and cosmic dynamics; general physics; chemistry; physics; mechanics; anatomy and general physiology; human physiology; vegetable physiology; medicine, pathology, pharmacology, and therapeutics; geology, mineralogy, and meteorology; agronomy; industry; social economics; mathematics; philology; education; pyrotechnics and ballistics; miscellaneous.

According to Baudrimont this was a very easy matter. One can master any subject in two years and consequently twenty subjects will only take forty years. This would be simple enough if one did not have to earn his own living; but Baudrimont did have to, so one must consider this showing as remarkable. Of course Herbert Spencer did something similar; but he is recognized as having been a remarkable man.

Before he was thirty, Baudrimont published a book entitled "Introduction à l'Étude de la Chimie par la théorie atomique;" but this was considered so revolutionary that he was forced to leave the Collège de France where Thénard had given him a position. In 1838 Baudrimont became a candidate for the chair of chemistry in the school of pharmacy, his chief opponent being Dumas. Baudrimont's criticism of Dumas' topic was so scaring that it prevented Baudrimont from getting any chair in Paris either then or later and he was forced eventually to accept a call to Bordeaux where he remained the rest of his life.

The latter part of this pamphlet is taken up with extracts from the works of Baudrimont, a very desirable thing because the originals are scarcely accessible. *Wilder D. Bancroft*

Annual Survey of American Chemistry. Vol. II. Edited by Clarence J. West. 22 × 14 cm; pp. 415. New York: *The Chemical Catalog Company*, 1927. Price: \$3.00. The first volume was criticized rather severely last year by the reviewer (31, 1278). The same remarks apply to this volume and there are now more people who share the reviewer's viewpoint. Unless these volumes are changed radically, it will not be long before everybody will be apologizing for them. The individual writers have been selected with care and have done their thankless tasks as well as could be expected.

The reviewer was much interested in the paragraph by Withrow, p. 115. "One of the most interesting achievements which have come to the attention of the writer during the year has been the manufacture of smoked salt. The salt used in pickling is smoked before use in pickling meat, thereby securing a greater penetration of smoke ingredients into the meat than in the normal practice of true smoking. It looks as though a revolutionary improvement in meat "smoking" were thus available. The product of this process when properly conducted has a golden brown color with a delicious smoked bacon or ham odor and taste. It can be readily distinguished in many ways and particularly by its odor and taste from numerous substitutes already appearing on the market which consist merely of salt treated with a filtered pyroligneous acid, followed by drying or evaporation. Contrary to superficial expectation the two products are not at all alike even in flavor. The manufacture of true "smoked salt" as distinguished from the imitation "smoked-salt" has reached a production amounting to many thousands of tons and is a rapidly growing business."

Wilder D. Bancroft

THE DETERMINATION OF THE ζ -POTENTIAL ON CELLULOSE.—
A METHOD*

BY DAVID R. BRIGGS

Electrokinetic Phenomena

The colloid electrical effects were named by Freundlich¹ "electrokinetic phenomena," to distinguish them from a kindred though not determinate phenomenon, the "thermodynamic potential," which exists also across the interface.

The electrokinetic properties are very closely related to other colloid properties. Adsorption, interfacial tension, flocculation, etc., are kindred phenomena and may, at least in some instances, be partially explained in terms of the electrical potential difference existing at the interface, and of which the electrokinetic phenomena are a means for measurement. Freundlich has shown recently that such measurements, which deal with the so-called ζ -potential, do not tell the whole story. As will be pointed out later, the ζ -potential measurements may not deal with the actual interface primarily, but with the fixed and movable layers of one of the phases in the immediate environment of the interface. However, the conditions extant in the interface will have in most cases, a determining influence upon these so closely adjacent layers, and we may reasonably expect to find significant differences by the utilization of these measurements, which are as fundamental, and probably more so, as are those obtained from adsorption measurements.

The more common methods for determining the charge on a colloidal particle are by means of the cataphoresis and electrosmosis phenomena. These methods are well known and have been utilized extensively for comparative measurements of the charge on such various colloidal materials as are readily adaptable to the conditions of such experiments. After considerable experimental investigation, it was found that to use either method for measuring the ζ -potential on cellulose would be undesirable.

Kruyt² and Freundlich³ and Rona have recently published papers describing their determinations of the ζ -potentials on capillary glass tubes by the streaming-potential method, wherein a liquid was forced through the tube under a measured hydrostatic pressure and the electromotive force set up across the tube was measured by potentiometric means. They found that the observed electromotive force was independent of the area of cross section or length of

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¹ Freundlich: "Colloid and Capillary Chemistry," (1926).

² Kruyt: Kolloid-Z., 22, 81 (1918).

³ Freundlich and Rona: Sitz. preuss. Akad. Wiss., 20, 397 (1920).

the tube. For a given liquid, the electromotive force observed, varied directly with the hydrostatic pressure and varied with the kind of glass, but *was constant for all sizes and shapes of tubes prepared from the same sample of glass.* It is by an adaptation of this method, modified to make possible its use on materials of such nature as paper pulp, that the measurements upon which the present paper is based were made.

The charge on a colloid is due to the presence of an electrical double layer in which, we must assume, "the electrical forces are arranged in equilibrium with osmotic or other forces present, so as to be a minimum." Michaelis⁴ ⁶ considers that there are three fundamental sources of this electrical double layer. Two are to be considered as examples of the action of forces with which we are familiar elsewhere in chemistry and physics. First, the forces of residual valencies which cause oriented adsorption, and second, the forces of dissociation which cause exchange adsorption. The third, Michaelis says, is due to the spontaneous distribution of ions at the free surface and comes into play in those cases where the electrical double layer is set up at the boundary of substances which are totally unreactive chemically, and are incapable of dissociation.

An example of the first case is that of AgI precipitated in an excess of either the Ag⁺ or I⁻ ions. The surface valencies of the crystals are unsatisfied. There are both Ag and I atoms on the surface, and these will show a selective attraction for ions of opposite charge in solution, and the crystal will thus take on a positive or negative charge depending upon which ion, Ag or I, may be in excess in the solution. The iso-electric point need not be at the point of exact neutralization of Ag⁺ and I⁻ ions in solution, however.

Of the second type, i.e., exchange adsorption, "there is a large number of evidently heteropolar compounds, peculiarly prone to electrolytic dissociation, in which one of the ions resulting from the dissociation is incapable of existence in the molecularly dispersed dissolved state." An example is silicic acid or a silicate. With silicic acid the dissociation tendency is the same as with any acid; however, the silicate ion does not disperse, but remains bound to the colloidal aggregate. The potential difference across the interface is a result of, and will be proportionate to, the dissociation tendency. (The degree of this tendency to dissociate depends upon the "intrinsic" natures of the solid material and of the liquid phase.)

The third class is illustrated by substances such as cellulose, collodion, or air bubbles. In these substances there is no oriented adsorption, nor is there a tendency to dissociate (certainly true in case of air bubbles). Yet a charge exists at the interface of these substances. This Michaelis explains as due to a difference in the capillary activity of H⁺ and OH⁻ ions. He assumes that the OH⁻ is more capillary active than the H⁺ ions and, therefore, the OH⁻ enters closer to the actual surface than the H⁺, thereby creating a zone of potential difference.

⁴ Michaelis: p. 471, "Colloid Chemistry," edited by J. Alexander (1926).

⁶ Michaelis: "Effects of Ions in Colloid Systems," (1925).

The characteristic features of "electrokinetic phenomena" are those of a heterogeneous system, one phase of which must be liquid and, in which, relative mechanical motion occurs between the different phases when they are subjected to an electrical field of force; or, when mechanical motion is brought about in either phase, an electrical field of force is set up in the system. To the first category belong the phenomena, *electrosmosis* and *cataphoresis*. In the first case, the liquid moves through a fixed diaphragm, while in the second, the colloidal particle moves through the liquid, under the influence of an electrical field. To the second group belong the *streaming potential* and *migration potential* (potential of falling particles) phenomena, wherein mechanical motion of the liquid or solid phase, respectively, gives rise to an electrical field of force in the system.

That solid materials immersed in water or other liquids show a difference of electrical potential across the interface has long been known. This, in fact, is to be expected from the first law of electrostatics, which states that all bodies coming into contact with each other become oppositely charged with electricity. Reuss⁶ in 1808, observed that when an electric current was passed through an earthenware diaphragm, water was transferred from the anode to the cathode chamber. In 1816, Porret⁷ described the same phenomenon when he used a sand diaphragm. Wiedemann^{8, 9} and Quincke¹⁰ made quantitative measurements of this electro-endosmosis phenomenon, and Quincke first showed that the water might travel in either direction depending upon the nature of the solid used, an observation which led him to the theory of the existence of an electrical double layer across the interface, the sign of which might be differently arranged for different substances. The theory of electrosmosis was first quantitatively expressed by Helmholtz^{11, 12}, and later by Perrin,^{13, 14} by Lamb,¹⁵ and by Smoluchowski¹⁶ without radical change.

Helmholtz developed his equation from the consideration of a single capillary tube of the solid material filled with the liquid and placed in an electrical field. He assumed the electrical double layer coating on the tube to be essentially a condenser, the plates of which were separated by a distance equal to the diameter of one molecule. Perrin¹³, following a suggestion of Pellat, introduced the dielectric constant of the liquid as a factor in the formula and thus made possible the assumption of a greater distance between the layers, than that assumed by Helmholtz.

⁶ Reuss: Mém. Soc. de Moscou, 2, 327 (1809).

⁷ Porret: Gilbert's Ann., 66, 272 (1816).

⁸ Wiedemann: Pogg. Ann., 87, 321 (1852).

⁹ Wiedemann: Pogg. Ann., 99, 177 (1856).

¹⁰ Quincke: Pogg. Ann., 113, 513 (1861).

¹¹ von Helmholtz: Wied. Ann., 7, 337 (1879).

¹² von Helmholtz: Gesamte Abhandlungen, 1, 855 (1882).

¹³ Perrin: J. Chim. phys., 2, 601 (1904).

¹⁴ Perrin: J. Chim. phys., 3, 50 (1905).

¹⁵ Lamb: B. A. Rep., 1887, 495.

¹⁶ von Smoluchowski: Bull. Acad. Sci. Cracovie, 1903, 182.

The following development of the electro-endosmosis formula is essentially that given by Perrin. Assume a single capillary acting as a diaphragm, across the ends of which is imposed an electrical potential difference. Further, assume the existence of an electrical double layer along the walls of the capillary, one layer of which is fixed tightly to the solid phase, while the other is located at a distance (δ) from the first, and in the liquid phase, being free to move. When an electrical field is set up due to an applied potential difference at the ends of the capillary, one charge tends to move in one direction, while the other tends to move in the opposite direction. The charge on the solid being fixed, the charged liquid layer will be moved along the surface of the capillary at such a rate that the frictional forces (R) are at equilibrium with the electrical forces (E).

The electrical force (E) acting on unit area of surface equals the product of the charge (e) on the double layer per unit of surface, and the applied potential difference (H) over unit length.

$$E = eH$$

At equilibrium, this must be equal to the frictional force (R) which it has overcome or balanced,

$$R = \Delta\eta,$$

where η = coefficient of viscosity and Δ = the decrease in velocity of flow of the liquid in a direction perpendicular to the wall of the capillary, that is, the average velocity of the layer of liquid taken between the layer of maximum velocity (u) and the layer of no motion, i.e., the fixed surface.

Then $\Delta = u/\delta$ where (δ) = the distance between the fixed and moving layers and

$$R = \eta u/\delta.$$

The maximum velocity (u) will be the velocity at which the liquid leaves the capillary, since the main body of the liquid in the capillary will move at the same rate as the layer near the wall. (u) may be measured then, by measuring the volume flowing in a given time and the diameter (or area of cross section) of the tube. Volume (v) emitted in given time then, is, where (r) is the radius of the capillary,

$$v = \pi r^2 u$$

then

$$R = \eta v/\delta \pi r^2$$

therefore,

$$eH = \eta v/\delta \pi r^2$$

Helmholtz and Perrin regarded the double layers as flat surfaces lying parallel to each other and at a distance apart (δ). These surfaces can, therefore, be thought of as the two plates of a flat condenser. The capacity (C) of a flat condenser is directly proportional to the quantity (Q) of electricity it holds and inversely as the P. D. (ζ) across the plates, i.e., $C = Q/\zeta$. Also, the capacity of a condenser, by a law in physics, is directly proportional

to the dielectric constant (ϵ) of the material separating the plates, and to the area (A) of the plates, and inversely proportional to their distance apart (δ), and to a constant (4π), that is,

$$C = \frac{\epsilon A}{4 \pi \delta}$$

then

$$\frac{Q}{\zeta} = \frac{\epsilon A}{4\pi\delta} \text{ or } \zeta = \frac{4\pi\delta Q}{\epsilon A}$$

but

$$Q/A = e, \text{ the charge per unit area.}$$

and

$$\zeta = \frac{4\pi\delta e}{\epsilon} \text{ or } \pi\delta = \frac{\zeta\epsilon}{4e}$$

substituting

$$eH = \frac{\eta v 4e}{\zeta \epsilon r^2}$$

then

$$v = \frac{r^2 \zeta H e}{4\eta} \text{ and } \zeta = \frac{4v\eta}{r^2 H e}$$

But, in a diaphragm, the area of cross section (q) takes the place of (πr^2) in the capillary, and $r^2 = q/\pi$,

then

$$v = \frac{q \zeta H e}{4\pi\eta}$$

and

$$\zeta = \frac{4\pi v \eta}{q H e}$$

$H = El$, where E = applied E. M. F. across diaphragm, and l = distance between ends of diaphragm.

$E = iw$, where (i) is the current and (w) the resistance, and $w = l/q\kappa$ where l = length of capillary, q = cross section area, and κ = specific conductivity of the liquid.

Whence,

$$v = \frac{\zeta i \epsilon}{\pi \eta \kappa}$$

and

$$\zeta = \frac{4\pi \eta \kappa v}{i \epsilon}$$

This equation states that where the electric current (i) is kept constant, the volume of liquid (v) which will flow in a given time through the diaphragm is directly proportional to the ζ -potential across the interface and to the dielectric constant (ϵ) of the liquid and inversely proportional to the viscosity (η) and specific conductivity (κ) of the liquid, but is independent of the area of cross section or length of the capillary.

We may now consider the electromotive forces produced by the flowing of a liquid through a capillary tube or a porous diaphragm. This phenomenon is in a sense the opposite to electrosmosis. In the latter, an external electromotive force causes the flow of water through the fixed diaphragm while in the former, the mechanical flow of water sets up an electromotive force across the two ends of the diaphragm. Beetz¹⁷ gave the name "Strömungsströme" to the electric current so generated, hence came the name "streaming potential" for the E. M. F. observed across the diaphragm under such conditions. This subject has been studied experimentally by Quincke,^{18, 19} Zollner,²⁰ Edlund,^{21, 22} Haga,^{23, 24} Clark,²⁵ Dorn,²⁶ and Elster,²⁷ the general observation being that the E. M. F. obtained was proportional to the pressure applied. The phenomenon is ascribed as due to a kind of electrical convection, and to be the result of the electrified layer of the liquid carrying its charge along with it as it moves through the capillary. In the case of a straight capillary, this results in a difference of potential becoming manifest at the two ends of the tube, which is compensated, if by no other means, by conduction backwards through the column of liquid in the tube. The simplest example of streaming potential is that in which a liquid is streamed past one electrode immersed in the liquid, while no motion of the liquid occurs around the other electrode.

Helmholtz¹¹ in his well known paper on interface potentials, first treated the subject mathematically. The following derivation of the streaming potential formula is that given by him.

He again considers the simpler case of a single tube filled with a liquid which is being forced through the tube under a hydrostatic pressure and across the interface, solid-liquid, of which there exists a potential difference. Let (e) denote the electrical density of the movable layer at a distance (δ) from the wall of the tube. The value of the velocity of motion (μ) of the liquid at the wall of the tube being zero, then the value of (μ) at the distance (δ) will equal

$$\mu = \partial\mu/\partial\delta \cdot \delta,$$

the infinitesimal rate of change of velocity with the distance component perpendicular to the wall, times this distance. The amount of electricity which is carried along by the liquid in unit time in the surface element $ds \cdot d\delta$ then will be

$$E_0 = e \cdot \partial\mu/\partial\delta \cdot \delta \cdot ds \cdot d\delta$$

Integrating a part of the expression through δ —

¹⁷ Beetz: Pogg. Ann., 146, 486 (1872).

¹⁸ Quincke: Pogg. Ann., 107, 1 (1859).

¹⁹ Quincke: Pogg. Ann., 110, 38 (1860).

²⁰ Zollner: Pogg. Ann., 148, 640 (1873).

²¹ Edlund: Pogg. Ann., 156, 251 (1875).

²² Edlund: Wied. Ann., 1, 161 (1877).

²³ Haga: Wied. Ann., 2, 326 (1877).

²⁴ Haga: Wied. Ann., 5, 287 (1878).

²⁵ Clark: Wied. Ann., 2, 335 (1877).

²⁶ Dorn: Wied. Ann., 10, 46 (1880).

²⁷ Elster: Wied. Ann., 6, 553 (1879).

$$\int e \cdot \delta \cdot d\delta = - \frac{1}{4\pi} \int_0^\infty \frac{\partial^2 \phi}{\partial \delta^2} = \frac{1}{4\pi} (\phi_i - \phi_a) \text{ or } \frac{1}{4\pi} \cdot \zeta$$

which, when the dielectric constant ϵ is considered becomes the same value as that obtained from consideration of the double layer as a condenser, as under electrosmosis,

$e\delta = \zeta\epsilon/4\pi$, where ζ is the P. D. across the interface. This is the "same value which the moment of the double layer would form if the opposing electricities of the system were all concentrated into the interface. So it results that the entire cross section of the tube of liquid carries along an amount of electricity in unit time"

$$E_0 = \zeta\epsilon/4\pi \cdot \int \frac{\partial \mu}{\partial \delta} ds$$

which is proportional to the P. D. across the interface, the dielectric constant of the liquid, the average velocity of the flowing liquid $\partial \mu / \partial \delta$ and to the surface of the layer (ds).

Integrating the latter expression of the above equation

$$\int \frac{\partial \mu}{\partial \delta} ds = - PA/\eta L$$

that is, the average velocity times the surface area of the tube is proportional to the hydrostatic pressure (P) and the area of cross section (A) and inversely proportional to the viscosity of the liquid (η) and to the length of the tube (L). This expression is a form of Poiseuille's Law governing the flow of liquids through capillary tubes. (The negative sign serves to indicate that the direction of flow of quantity E_0 is opposite to that of E_1 given below.) Then

$$E_0 = - \frac{PA\zeta\epsilon}{4\pi\eta L}$$

which is the amount of electricity which is carried along the tube per unit of time, and which would accumulate at one end of the tube if it were not for an electrical conductance through liquid in the tube in the opposite direction.

An electromotive force H , is thus created between the ends of the tube and the amount of electricity (E) which is conducted back through each area of cross section (A) in unit time will be

$$E_1 = HA/\sigma L$$

where (σ) is the specific resistance of the liquid.

If there is no other means of conductance than that through the column of liquid, an equilibrium will be established when

$$E_0 + E_1 = 0$$

then

$$\frac{H}{\sigma} = \frac{\zeta P \epsilon}{4\pi \eta} \text{ or } H = \frac{\zeta P \epsilon}{4\pi \eta \sigma}$$

This equation shows that the E. M. F. (H) observed when a liquid is forced through a capillary across the ends of which there is a difference of

hydrostatic potential (P), is directly proportional to (P), to the potential difference across the interface solid-liquid (ζ), and to the dielectric constant (ϵ) of the liquid. (H) is inversely proportional to the viscosity (η) of the liquid and to its specific conductivity (κ), but is *independent* of the *dimensions* of the tube or diaphragm, so long as the diaphragm material has *no conductivity in itself*. This equation was modified by Lamb²⁸ to include a term defining the slippage of the liquid layer along the face of the solid. However, this slippage is so small as compared with the relative motion of the liquid over the film of liquid which is in contact with the solid, that it is negligible.

It will be noted that the electrosmosis formula for the volume (v) flowing in unit time when the current (i) is kept a constant, and the streaming potential formula given above are both independent of the dimensions of the diaphragm.

$$v = \frac{\zeta i \epsilon}{4\pi\eta\kappa} \quad (\text{electrosmosis equation})$$

$$H = \frac{\zeta P \epsilon}{4\pi\eta\kappa} \quad (\text{streaming potential equation})$$

If these equations are correctly derived and no term is omitted from one which is considered in the other, the relation

$$v/i = H/P \text{ should hold.}$$

Saxen²⁹ determined with the same apparatus the electrosmotically transferred volume (v) and also the potential (H) for the streaming current. He used a clay plate for the diaphragm and, as liquids, solutions of zinc, cadmium and copper sulfates with electrodes of the corresponding metals so as to eliminate polarization disturbances. The values which he obtained show a very close approximation to the identity of these ratios when the other variables are held constant. Values for the ζ -potential obtained by either the electrosmosis or streaming potential method then should be identical.

Kruyt³ used the streaming potential method to study the comparative effects of electrolytes on the ζ -potential of a surface and on colloid stability. He used glass tubes of various lengths and areas of cross section, and streamed electrolytes of low concentration through them under measured hydrostatic pressure. He measured the E. M. F. set up across the ends of the tube by means of non-polarizable Ag-AgCl electrodes and a potentiometer, using a capillary electrometer as the null instrument. For a given sample of glass and a given liquid, he found the value H/P to be a constant, but to be different for different samples of glass. He points out that Grumbach³⁰ in some studies on the influence of non-electrolytes in a millimolar KCl solution upon the streaming potential, found that there was some change in the H/P value given, as the cell was allowed to set for a few days. Kruyt verified this observation, but found it so small as to be negligible for all practical purposes.

²⁸ Lamb: *Phil. Mag.*, (5) 25, 52 (1888).

²⁹ Saxen: *Wied. Ann.*, 47, 46 (1892).

³⁰ Grumbach: *Ann. Chim. Phys.*, (8) 24, 433 (1911).

Older experiments cited by G. de Villemontée³¹ stated that with solutions of copper, zinc and nickel sulfates, there was no streaming potential set up. The solutions used in these experiments contained 10 grams of salt per liter, however, and their conductivities were too high to allow any observable E. M. F. to be set up. There has been a good deal of data³²⁻³⁵ obtained by electrosmosis experiments which show that electrolytes, in general, decrease the ζ -potential on colloids, a fact that is of significance when we remember that electrolytes, in general, also decrease the stability of colloidal solutions.

Kruyt found that in very small concentrations of electrolytes, of the order of 100 μ mols per liter, KCl, HCl, and BaCl₂ increased (ζ) on glass, but quickly thereafter decreased it steadily in concentrations of the order of 200-1500 μ mols per liter, though never discharging it entirely. AlCl₃, the only trivalent metal he used, showed no indication of an increase of ζ , but in very low concentrations (less than 1 μ mol per liter) totally reversed the charge and maintained it reversed though approaching the value of zero again in higher concentrations.

Freundlich and his coworkers^{3, 36} made use of the streaming potential methods for determination of the ζ -potential on glass capillaries in their researches on the relationship between the "electrokinetic potential" and the "thermodynamic potential" of interfaces.

Borelius³⁷ was first to compare potentials measured tangentially to those measured perpendicularly to an interface. For his transverse measurements he used a paraffin diaphragm and salt solutions, and for the tangential measurements he took the cataphoretic measurement of Powis (loc. cit.) on paraffin oils.

Freundlich and Ettisch³⁸ used glass tubes for the tangential measurements on the ζ -potential and the thin glass electrode of Haber and Klemensiewicz³⁸ for the measurements of the ϵ -potential, i.e., the transverse potential. They showed that the ζ -potential was never more than a fraction of the ϵ -potential and that it was governed very largely by electrolyte conditions in the solution. The ϵ -potential was found to be entirely independent of the electrolyte concentration in the external solution with the exception of the H⁺ and OH⁻ ions. The glass electrode acts, then, as a hydrogen electrode. In order to explain this discrepancy between the two values, Freundlich points out³⁹ that it is necessary to make two assumptions. They are, first, the existence of a *diffuse* double layer in at least one of the phases (as postulated by Gouy^{40, 41}) which

³¹ de Villemontée: J. Phys., (3) 6, 59 (1897).

³² von Elissaff: Z. physik. Chem., 79, 385 (1912).

³³ Burton: Phil. Mag., (6) 11, 425 (1906); 12, 472 (1906); 17, 583 (1909).

³⁴ Ellis: Z. physik. Chem., 78, 321 (1912); 80, 597 (1912); 89, 145 (1915).

³⁵ Powis: Z. physik. Chem., 89, 91, 179, 186 (1915).

³⁶ Freundlich and Ettisch: Z. physik. Chem., 116, 401 (1925).

³⁷ Borelius: Ann. Physik, (4) 50, 447 (1916); 53, 239 (1917).

³⁸ Haber and Klemensiewicz: Z. physik. Chem., 67, 385 (1909).

³⁹ Freundlich: Trans. Faraday Soc., 1926, 440.

⁴⁰ Gouy: J. Phys., (4), 9, 457 (1910).

⁴¹ Gouy: Ann. Phys., (9), 6, 5 (1916); 7, 129, 149 (1917).

diminishes in intensity gradually in the direction away from the interface. The second is that a layer of the liquid is held tightly at the surface of the solid and that the motion tangent to the surface is between the movable liquid phase and this thin layer of liquid adhering to the wall. (ζ) then can be thought of as varying with the fraction of ϵ -potential which is actually moved; that is to say, perhaps only a small fraction of the total potential from a point inside the solid phase to a point inside the liquid phase (which is the ϵ -potential) will exist across the two layers of liquid, movable and non-movable, and this fraction is ζ . Also the sign of the potential across these two layers could be reversed by the action of electrolytes without appreciably changing the ϵ -potential. The ϵ -potential is to be thought of as a "thermodynamic"-potential and to be governed by the Nernst formula. The ζ -potential will tell nothing about the ϵ -potential; but the ζ -potential will be a closer function of adsorption and other colloid qualities of the system than will the ϵ -potential.

In Freundlich's investigation, the action of KCl, BaCl₂, La(NO₃)₃ and Th(NO₃)₄ upon the ζ -potential on his glass tubes was observed. KCl and BaCl₂ gave an increase in ζ in concentrations between 1 and 10 μ mols, and decreased it to nearly zero in 1000 μ molar solutions. The KCl curve on the graph lay well above the BaCl₂ curve. La(NO₃)₃ caused no increase in ζ , but a steady decrease to not quite zero in 1000 μ molar solution. Th(NO₃)₄ reversed the charge in a 1 μ molar solution and reached maximum reversal at 10 μ molar solution, then decreasing again to approximately zero in a 1000 μ molar solution. The change in the ϵ -potential for the same solutions was relatively small and steadily in one direction, all curves on the graph being virtually parallel.

Assumptions upon which the Electrosmosis and Streaming Potential Formulae are based

ϵ -The dielectric constant of the liquid in the region of an interface is assumed to be equal to that of the liquid in bulk. Recent measurements of the dielectric constant of water in presence of an electrical field show that ϵ for water can be lowered from a value of 80 to a value of 1 by placing the water in an electrical field of the order of 500,000 volts per centimeter.* Helmholtz and Quincke (loc. cit.) estimated the distance across an interface as of the order of 10⁻⁸ centimeter, that is, the thickness of one molecule. If the ζ -potential were then of an order of 0.2 volts, it is easily seen that the liquid in the interfacial layer is being acted upon by an extremely high electrical field and its dielectric constant might be greatly reduced. According to the theory of Gouy (loc. cit.) on the existence of a diffuse double layer, which postulates a much greater distance between the centers of electrical charge than that estimated by Helmholtz, it seems probable that the electrical field extant in interfacial regions may not be high enough to entirely

* Statement made by Debye in a lecture before the Minnesota Section of the American Chemical Society and Society of Sigma Xi, April, 1927.

eliminate (ϵ) from the equation. Probably the actual value for (ϵ) lies somewhere between 80 and 1, and it may vary with the conditions in the interface.

With dilute salt solutions, ϵ may not remain unchanged. Walden, Ulrich and Werner⁴² have offered evidence that the addition of a salt to a pure liquid first decreases ϵ and then, with increased concentration of salt, increases it to a value greater than that of the pure solvent. This is the regular thing with organic solvents, although with water they observed only the initial drop. Kruyt and van der Willigen⁴³ have drawn the conclusion that the so-called antagonism of ions probably depends upon the fact that one of the electrolytes shows a maximum in apparent ζ -potential with increasing concentration, which effect is probably due to its influence on the dielectric constant of the liquid. Univalent electrolytes usually show this maximum with increasing concentration, but its exact position is not predictable; polyvalent ions do not always show it.

It is possible that there may be other effects, also, on the liquid in the interface than those due to the electric field. For instance, the density of water at the interface may be different from water in bulk. Data obtained by Cude and Hulett,⁴⁴ Harkins and Ewing,⁴⁵ and Williams⁴⁶ show that there is a difference in the apparent density of charcoal in different liquids and they assume this to be due to differences in compressibilities of these liquids on the surface. Lamb and Coolidge⁴⁷ assumed the total heat of adsorption to be due to compression of liquid in the interface and calculated a pressure of 37,000 atmospheres as the compressing force exerted there. Rideal⁴⁸ refuses to believe that this effect will function to a greater distance from the surface of the solid than upon the monomolecular layer on that surface and explains the anomalous results obtained on charcoal densities as due to differences in the penetration (into the pores of the charcoal) or wetting properties of the various liquids.

η -The viscosity of the liquid is assumed to remain a constant for dilute salt solutions and to be equal to that of the pure liquid in the bulk. That the viscosity of the liquid in the interface does not vary from that value ordinarily given for the liquid is very probable, due to the fact that the viscosity measurements are themselves measurements of the resistance to shearing motion at an interface. However, it is possible that even in dilute solutions, (η) may be affected, due to adsorption of the electrolyte into the interface and a consequent increase in the effective concentration of the electrolyte in that part of the system. Helmholtz's and Perrin's equation leaves out of consideration, also, any effect due to slippage of the liquid layer

⁴² Walden, Ulrich, and Werner: *Z. physik. Chem.*, 116, 261 (1925).

⁴³ Kruyt and van der Willigen: *Versl. Kon. Akad. Wet. Amsterdam*, 34, 1240 (1926). (Cited by Kruyt, Roodvoets, and van der Willigen: *Colloid Symposium Monograph*, Vol. IV).

⁴⁴ Cude and Hulett: *J. Am. Chem. Soc.*, 42, 391 (1920).

⁴⁵ Harkins and Ewing: *J. Am. Chem. Soc.*, 43, 1794 (1921).

⁴⁶ Williams: *Proc. Roy. Soc.*, 98A, 223 (1920).

⁴⁷ Lamb and Coolidge: *J. Am. Chem. Soc.*, 42, 1146 (1920).

⁴⁸ Rideal: "Surface Chemistry", 176 (1926).

along the surface of the solid, assuming all motion to be between two liquid layers, where η would be the only factor. Lamb,³⁸ however, introduces a term, $1/\beta$, into all the equations of Helmholtz, where β = the coefficient of slippage at solid-liquid interface and l = linear magnitude of this slippage. This is not considered of importance in later treatments of the subject.

δ —The distance between the layers is not to be thought of as the actual distance between two plane surfaces as Helmholtz pictured it, but rather the distance between the electrical centers of gravity of two diffuse layers. Lippmann,⁴⁹ from considerations of the interfacial tension-voltage curve of mercury against sulfuric acid, as in a capillary electrometer, concluded (δ) was independent of the charge across the interface and of the sign of this charge. That this was an exceptional case was pointed out by Gouy⁴¹ who showed that δ was not constant and that the double layers were to be considered not as flat surfaces but as diffuse layers. This conception of the double layer finds its theoretical foundation in the kinetic theory of heat, which makes it very unlikely that all the ions would be distributed in a single plane in the liquid. (See also Billiter).⁵⁰ Rideal states, "At the beginning of the present century, when molecular magnitudes became more exactly known, it became apparent that δ was smaller than an atomic diameter. It was therefore suggested that the charges of the double layer must be regarded as separated by a dielectric medium. The thickness of the double layer is increased eighty fold if pure water be regarded as the intervening medium, but even if the dielectric constant of so thin a layer be considered less than that of water in bulk the thickness will still be of a possible order of magnitude. The variations in δ may thus be attributed to a variation either in the thickness of the double layer or in the effective dielectric constant, or to a combination of both."⁵¹

δ , the distance between the double layers, then, is variable, and may, in cases where polyvalent ions or other very capillary active ions are present in the solution, become so small as to exclude any great relative motions in the two layers, causing an anomalous lowering of ζ -potential.

In the derivation of the equations for the determination of ζ it will be remembered that (δ), the distance between the electrical double layers, was equated to (δ), the distance between the layer of no motion and the layer of maximum velocity. It is very unlikely that these distances will be identical or that they will vary in the same manner and degree with changes in the environment. It seems probable that herein lies the principal fallacy inherent in these equations. However, at present it cannot be eliminated.

κ —The specific conductivity factor found in the equation refers to that of the liquid. In the derivation of the streaming potential formula it will be remembered that the solid phase is assumed to have a negligible amount of

⁴⁹ Lippmann: Sitz. Akad. Wiss. Berlin, p. 947 (1881), (Cited by Rideal: "Surface Chemistry", p. 211).

⁵⁰ Billiter: Z. physik. Chem., 45, 307 (1903).

⁵¹ Rideal: "Surface Chemistry", 212 (1926).

conductivity. Also any "surface conductance" is disregarded. Smoluchowski⁵² has pointed out that "surface conductivity" might become an important factor in electrokinetic measurements when the conductivity of the liquid was very low. It would become negligible in salt solutions of concentrations high enough to give the liquid phase an appreciably high conductivity. Stock⁵³ noted that quartz powder in such liquids as nitrobenzene, aniline, etc., greatly increase the apparent conductivity of these liquids. McBain⁵⁴ mentions experiments by Darke on the conductivity of dilute KCl in a quartz capillary which showed conductivity over that of the solution in bulk. From these considerations, he stated that Darke was attempting to make absolute measurements of electrosmosis, none of which had previously existed so far as he (McBain) knew. Fairbrother and Mastin⁵⁵ performed experiments which indicated a small increase in the apparent conductivity of dilute aqueous electrolytes in a porous diaphragm over that in bulk. These authors offer a method for electrosmosis determinations of ζ , in which they eliminate this source of error by measuring the "cell constant" of the diaphragm employed, using N/10 KCl solution, in which they assume the "surface conductance" to be very small in comparison with the "bulk conductance." Stamm⁵⁶ found that water used in electrosmosis experiments on wood sections had a specific conductivity of 5.43×10^{-6} mho, while the specific conductivity of the average transverse section of the wood impregnated with this water was 8.27×10^{-6} mho. This indicated that the actual water in the wood had a specific conductivity of perhaps 2 or 3 times that in bulk.

In the derivation of the streaming potential formula the quantity of electricity which is conducted back through the liquid in the tube in unit time, is

$$E_L = \frac{HA}{\sigma L} = \frac{H\pi r^2 \kappa_L}{L}$$

This is true when the conductivity (κ_L) is uniform over the whole area (πr^2) of the cross section of the tube and equal to the conductivity of the liquid in bulk. When the conductivity is changed in the region of the interface, a new term must be introduced to take care of this variation.

Let (R) denote the radius of the column of liquid (in the tube) in which the conductivity is that of the liquid in bulk, and (δ) be the distance perpendicular to the wall in which the conductivity is changed, and in which the average conductivity is κ_s . The total radius of the tube then will be $R + \delta$. The amount of electricity (E_s) conducted through the volume adjacent to the wall (i.e., the surface conductance) equals

⁵²von Smoluchowski: *Physik. Z.*, 6, 529 (1905); *Anz. Akad. Wiss. Krakov*, 1903 A, 185.

⁵³Stock: *Anz. Akad. Wiss. Krakov*, 1912, A, 635. (Cited by Stamm: *Colloid Symposium Monograph*, Vol. IV, p. 246).

⁵⁴McBain: *Trans. Faraday Soc.*, Joint Symposium of Faraday and Physics Societies, 1921, 150.

⁵⁵Fairbrother and Mastin: *J. Chem. Soc.*, 125, 2319 (1924).

⁵⁶Stamm: *Colloid Symposium Monograph*, 4, 246 (1926).

$$E_s = \frac{H(\pi R^2 - \pi R^2 + \pi R\delta + \pi\delta^2)}{L} \cdot \kappa_s$$

$$= \frac{H\pi}{L} (R\delta + \delta^2) \kappa_s$$

The amount of electricity carried by the bulk of liquid will be

$$E_L = \frac{H\pi R^2 \kappa_L}{L}$$

where κ_L = the specific conductivity of the liquid in bulk.

The total amount of electricity conducted then, is

$$E_T = E_L + E_S = (H\pi/L) [R^2 \kappa_L + (R\delta + \delta^2) \kappa_s]$$

When the specific conductivity of the liquid (κ_L) is employed, the equation given above for the streaming potential will hold only when there is no surface conductance; otherwise the dimensions of the tube must appear in the equation. That the surface conductance was negligible in the case of glass tube experiments with streaming potential as carried out by Kruyt and by Freundlich (loc. cit.) is evidenced by the constant value of H/P which they obtained with any given sample of glass regardless of the dimensions of the tube.

If we could consider the diffuse double layer of Gouy (loc. cit.) as extending to the center of the capillary, then the value of R in the equation given above would become equal to zero and

$$E_T = \frac{H\pi\delta^2\kappa_s}{L}$$

would denote correctly the quantity of electricity flowing back through the tube in unit time. If we could then measure the average conductivity of the liquid (κ_s) in the tube or diaphragm, an absolute value of ζ would be obtainable by the streaming potential method. Gouy calculated the values of δ for a surface, the charge over unit area of which amounted to 10 electrostatic units, and obtained the following: (in these values, δ -stands for the electrical center of gravity of the diffuse layer)

| | | δ |
|------------|----------------|-----------------|
| Solutions | N/100 in ions | - 0.96 $\mu\mu$ |
| Solutions | N/1000 in ions | - 9.6 $\mu\mu$ |
| Pure water | (Kohlrausch) | - 1010 $\mu\mu$ |

For low potentials and dilute solutions, then, δ may attain a considerable value (compared with molecular dimensions), even comparable to the radius of the tubes in a tightly packed diaphragm. Determination of the value (κ_s) may be made according to the method of Fairbrother and Mastin (loc. cit.) by measuring the "cell constant" for the diaphragm with N/10 KCl solution and calculating the specific conductivity of any other liquid which may be streamed through it. The surface conductance in the case of N/10

KCl solution would be very low, as they pointed out, in comparison to the bulk conductivity. Gouy's values for the thickness of the surface conducting layer (δ) in a N/10 solution also bear out this conclusion.

Another assumption which we must make when we use this equation for the streaming potential, is that the conditions of the capillaries of the diaphragm do not differ much from those postulated for the simple capillary pictured in the process of derivation of the equation. Poiseuille's Law holds for simple cylindrical capillaries of not too large diameter, and with pressures low enough not to cause turbulent flow. We must assume that it also holds for the average capillary of the diaphragm and must use pressures low enough so that turbulent flow is not produced.

That the ζ -potential appears to have a temperature coefficient is indicated by work of Cruse⁶⁷ who found that with a clay diaphragm and distilled water, a maximum was obtained for (ζ) at a temperature of 40°C. Smoluchowski⁶⁸ claimed this change to be due to the fact that the factor $\eta\kappa/\epsilon$ did not remain a constant with change of temperature. Briggs, Bennett, and Pierson⁶⁸ say that their investigations show that the change in rate of volume flow in electrosmosis experiments is a function of the viscosity change with temperature, and that no maximum occurs. Cruse's results, they claim to be due to the failure of the diaphragm to come to equilibrium with the liquid before the readings were taken. Gee and Harrison⁶⁹ measured the value of (κ) with change in temperature for the water they used, adopted values of (η) from Landolt-Börnstein and values of (ϵ) given by Drude, and obtained for temperatures ranging between 15° C. and 80° C., values for $\eta\kappa/\epsilon$ which were very close to a constant, thus indicating that the variation observed by Cruse was due to a variation in (ζ). It is of interest that Gee and Harrison should observe a like maximum of the ζ -potential on wool, cotton, and silk fibers at approximately the same temperature as that of Cruse on clay, i.e., 35°C.-40°C.

The ζ -potential on Cellulose

Scattered instances of ζ -potential measurements on cellulose have been made by means of the electrosmosis methods. Perrin^{13, 14} in his studies upon the influence of dissolved electrolytes on various colloids, found that in an electrosmosis apparatus in which the voltage drop was 10 volts per centimeter, a diaphragm of cotton fibers 1.4 centimeters in cross section gave the following values for the rate of flow in acid and alkali concentrations:

| | | | |
|-------|-----|--------|------------|
| N/50 | HCl | 0 cc. | per minute |
| N/500 | HCl | 20 cc. | " " |
| N/500 | KOH | 70 cc. | " " |

Larguier des Bancels⁶⁰ showed that the negative charge on cellulose increased in alkali solutions and decreased in acid solutions, and, also, that polyvalent positive ions (Ca, Zn, Ba) decreased this charge while polyvalent negative ions (SO₄ and Fe(CN)₆) increased it.

⁶⁷ Cruse: *Physik. Z.*, 6, 201 (1905).

⁶⁸ Briggs, Bennett, and Pierson: *J. Phys. Chem.*, 22, 256 (1918).

⁶⁹ Gee and Harrison: *Trans. Faraday Soc.*, 6, 42 (1910).

⁶⁰ des Bancels: *Compt. rend.*, 149, 316 (1909).

German Patents⁶¹ note the migration of cellulose fibers toward the positive pole under stress of an electrical field, but no measurements of this effect are given.

In all instances, no attempt is made toward obtaining absolute values for the charge at the interface. They give only comparative values which show qualitatively the effects which electrolytes have on the charge, values which are not necessarily duplicable even when the same sample of cellulose is used again.

Gee and Harrison,⁶² and Harrison,⁶³ in developing their electrical theory of dyeing, used the streaming potential method for determining the ζ -potential on cotton, silk, and wool fibers against pure water and against solutions of various electrolytes and dyestuffs. A description of the apparatus used, is given in the second paper referred to. They found that: (a) acids increase the charge on a positively charged fiber and decrease it on a negatively charged fiber; (b) all acids act the same when the H ion concentration is the same; (c) bases act oppositely to acids; (d) when a salt is used as the electrolyte, ions of the opposite charge to that of the fiber have the most effect and the charge may be reversed by such ions; (e) polyvalent ions have greatest effects; and (f) the charge on a negative fiber (cotton, wool, silk) against water is greatest at the temperature of 40°C.

In their measurements they packed the fibers into a cell between two platinum electrodes and measured the electromotive force set up when the liquid was forced through this diaphragm. Due to a polarization of electrodes, they could not use an ordinary potentiometer, but had to measure the electromotive force in a manner which called for no flow of current through the electrodes. This they accomplished by charging a condenser from the streaming potential cell and then measuring the discharge of this condenser through a ballistic galvanometer. They measured the specific conductivity of the liquid by a conductivity cell arranged to utilize the liquid after it had passed through the diaphragm. These measurements are the most accurate made on cellulose and approach more nearly absolute measurements than those made by use of the electroosmosis method.

Development of Method

From a consideration of the results obtained by Krutz³ using capillary glass tubes and the streaming potential method for the determination of ζ , it was thought that similar results might be obtained by packing cellulose tightly into a compartment between two electrodes and forcing a liquid through it. Krutz obtained constant values of H/P which were independent of the dimensions of the glass tube. The values for H/P, using cellulose as a diaphragm, should likewise be constant and independent of the tightness with which it might be packed.

⁶¹ Graf von Schwerin und Farbwerke vorm. Meister, Lucius, and Brünning. D. R. P. 124509, 124510, 128085.

⁶² Harrison: *J. Soc. Dyers and Colourists*, 27, 278 (1911).

Accordingly, an apparatus was prepared and such measurements were attempted. As a cell, the apparatus illustrated in Fig. 1 was used. This cell had previously been used in electrosmosis experiments, and was virtually a U-tube with a chamber (C) in the horizontal section which could be filled with fibers, these being retained at each end by a porous platinum disk (D and D'). The platinum electrodes (E and E') which were formerly connected with a source of potential could now be used to conduct off any potential which might be brought about due to the motion of the liquid through the diaphragm. The liquid was forced through the cell in a direction from A

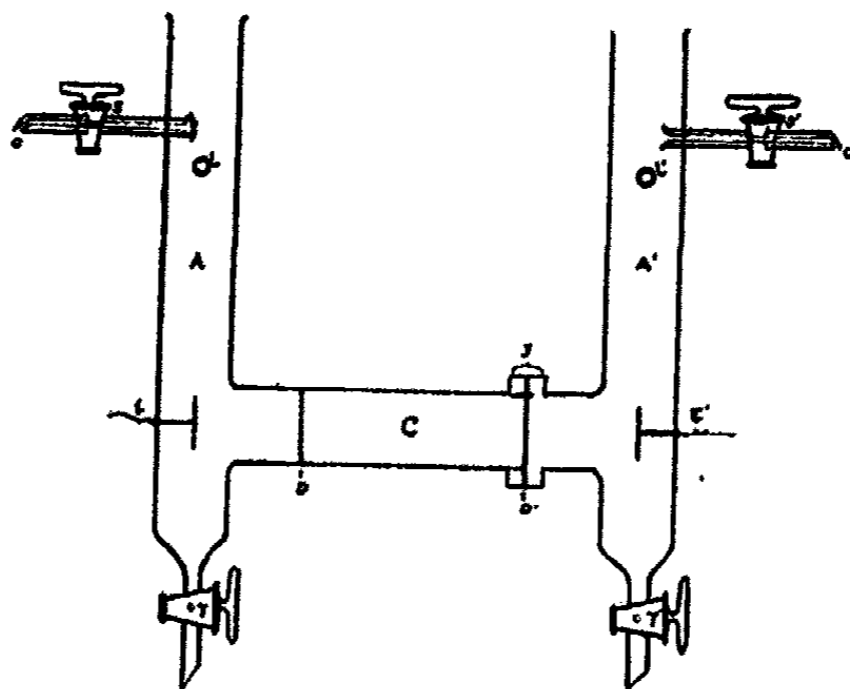


FIG. 1

to A', the disk D' being clamped between the jaws of the two halves of the cell, and therefore, able to withstand considerable pressure without distortion.

It was with this cell that an attempt was made to use a Leeds and Northrup Potentiometer (Type K) to measure the potential set up across the diaphragm, but it was found that the polarization of the electrodes made accurate measurements impossible. Calomel half cells, which are nonpolarizing, were then connected to the cell through the tubes and stopcocks (T and T'), but the added resistance offered by the longer path through water made it impossible to get enough current through to cause deflection in the galvanometer. It was then that the quadrant electrometer was substituted as the voltage measuring apparatus, and polarization troubles were decreased to a minimum, the original platinum electrodes being used.

For all preliminary experiments, the liquid used was distilled water caught directly from the still and having a specific conductivity of the order of 3×10^{-6} mhos. For diaphragm material, a bleached sulfite pulp which had been electrolyzed free of ash (ash content of order of .02 per cent) was used. This pulp was kept wet in an airtight container until ready to be used.

Among the first experiments, it was found that the ratio H/P was not a constant with variation in P unless the diaphragm was packed tightly enough

so that the higher pressures could cause no appreciable decrease in the volume occupied by the pulp. The following tables show this effect. Table I (a) shows results with a diaphragm of pulp only fairly tightly packed, and Table I (b) and (c) for a tight and a very tight diaphragm, respectively.

TABLE I (a)

Streaming Potential to Pressure Ratio not a Constant
for Different Diaphragms of Cellulose

| P (cm.Hg.) | H (mv) | H/P |
|---------------|-----------|------|
| 51.6 | 130 | 2.52 |
| 37.9 | 107 | 2.82 |
| 28.5 | 89 | 3.12 |
| 16.0 | 52 | 3.25 |
| 10.2 | 32.5 | 3.14 |

TABLE I (b)

| | | |
|------|-------|------|
| 51.5 | 106.0 | 2.06 |
| 29.0 | 62.5 | 2.15 |
| 10.0 | 21.5 | 2.15 |

TABLE I (c)

| | | |
|------|------|------|
| 51.9 | 81 | 1.56 |
| 38.9 | 62 | 1.59 |
| 26.4 | 43 | 1.63 |
| 10.0 | 15.8 | 1.58 |

These tables show another effect, that is, the value H/P, while it may be a constant for any given diaphragm does not remain a constant for diaphragms of different pore dimensions. This is shown also in Table II. Since the value

TABLE II (a)

Streaming Potential not a Function of Rate of Flow for Different Diaphragms
at Same Hydrostatic Pressures

| | P (cm.Hg.) | H (mv) | H/P | R (cc./sec.) | H/R | $\frac{H^2}{P \times R}$ |
|----|---------------|-----------|------|-----------------|-----|--------------------------|
| A. | 51.9 | 81 | 1.56 | .243 | 329 | 512 |
| B. | 51.9 | 95 | 1.83 | .309 | 308 | 562 |
| C. | 51.9 | 113 | 2.09 | .455 | 249 | 520 |
| D. | 51.9 | 127.5 | 2.46 | .575 | 222 | 545 |
| E. | 51.9 | 139.0 | 2.68 | .650 | 212 | 567 |

TABLE II (b) (with KCl solution)

| | | | | | | |
|----|------|----|------|------|----|------|
| A. | 50.5 | 25 | .495 | .312 | 80 | 39.6 |
| B. | 50.3 | 27 | .538 | .410 | 66 | 35.5 |
| C. | 50.1 | 32 | .638 | .695 | 46 | 39.4 |

TABLE II (c)

| | | | | | | |
|----|------|-----|------|------|-----|-----|
| A. | 48.4 | 98 | 2.03 | .298 | 329 | 668 |
| B. | 46.2 | 101 | 2.19 | .236 | 427 | 934 |
| C. | 47.6 | 120 | 2.52 | .390 | 308 | 776 |
| D. | 48.2 | 125 | 2.60 | .405 | 310 | 806 |
| E. | 48.0 | 134 | 2.79 | .556 | 241 | 672 |
| F. | 47.9 | 145 | 3.04 | .758 | 192 | 584 |

TABLE II (d)

| | | | | | | |
|----|------|-----|------|------|-----|-----|
| A. | 50.2 | 105 | 2.09 | .357 | 294 | 614 |
| B. | 50.2 | 122 | 2.43 | .472 | 259 | 630 |
| C. | 50.2 | 125 | 2.49 | .595 | 210 | 521 |
| D. | 50.2 | 131 | 2.61 | .595 | 220 | 572 |

H/P was not constant for various degrees of packing, it seemed evident that this must be due to one of the following causes. Either there was a change in the conductivity with change in tightness of packing, or else the rate of flow of the liquid through the pulp came in some way into the equation. Table II shows results of an experiment made to find whether or not rate of flow (R) played any part. These results are obtained with diaphragms of different tightness of packing, using a uniform pressure (P) on each.

In all experiments shown in Table II, the tightest packing of the pulp occurs as (A) and is progressively less tightly packed as we proceed down the table. In Table II (a) it appeared that the factor $H^2/P \times R$ was almost a constant, but the other experiments reversed this indication. Table III strengthens the conclusion that rate of flow does not play any determining part in the phenomenon. Table III shows a series of observations on the same diaphragm, at different pressures. The packing was tight enough to make H/P constant at these varying pressures.

TABLE III

Streaming Potentials not a Function of Rate of Flow for Given Diaphragm at Different Hydrostatic Pressures

| P (cm.Hg.) | H (mv) | H/P | R (cc./sec.) | H/R | $\frac{H^2}{P \times R}$ |
|---------------|-----------|------|-----------------|-----|--------------------------|
| 55.2 | 141 | 2.56 | .481 | 293 | 750 |
| 47.9 | 122 | 2.55 | .424 | 283 | 722 |
| 38.7 | 100 | 2.58 | .343 | 292 | 754 |
| 28.2 | 75 | 2.66 | .238 | 315 | 838 |
| 17.8 | 48.6 | 2.79 | .149 | 332 | 926 |
| 7.5 | 21.5 | 2.86 | .060 | 359 | 1028 |
| 47.5 | 118.0 | 2.47 | .424 | 279 | 690 |
| 38.4 | 98.0 | 2.55 | .338 | 290 | 742 |

Table III shows also, that rate of flow is proportional to pressure for a given diaphragm (there was a slight constant error made in this series of observation of pressure which became especially noticeable in low pressures).

These experiments indicated that (R) the rate of flow could not be utilized in obtaining a constant factor in streaming potential measurements. The other alternative, as mentioned above, was that the conductivity of the diaphragm was changing with tightness of packing. It was inconceivable that cellulose was acting as a conductor, and yet, when the amount of cellulose packed into a unit volume was increased, the H/P ratio decreased—a seeming indication that κ , the specific conductivity, was increasing. In Table II (b) a KCl solution was used. It was thought that the packing effect, if it was due to a difference in conductivity, would be very much reduced or disappear in a KCl solution, where the conductivity of the liquid was much higher than in the case of the distilled water. Table II (b), however, showed the packing effect as before. The work of Kruyt on glass tubes was repeated to see if, indeed, the value H/P was independent of the size of the capillary. Table IV shows the results of such an experiment, where tubes of the same glass but of four different sizes of cross section and length were used, and at various pressures. The rate of flow (R) is given to indicate the large difference in size of cross section of these tubes. The results of Kruyt are verified and the streaming potential thus shown to be independent of the size of the pores of the diaphragm.

TABLE IV
Streaming Potential to Pressure Ratio Constant for Glass Tubes
of Various Dimensions

| Tube No. | P (cm.Hg.) | H (mv) | H/P | R (cc./sec.) |
|----------|---------------|-----------|-----|-----------------|
| A | 30.5 | 4370 | 143 | 1.56 |
| | 22.0 | 3100 | 141 | 1.21 |
| | 14.4 | 2140 | 147 | 0.89 |
| B | 15.5 | 2250 | 145 | 0.22 |
| | 26.75 | 3710 | 139 | 0.30 |
| C | 27.65 | 3630 | 137 | 1.56 |
| | 19.40 | 2700 | 139 | 1.35 |
| D | 13.70 | 1990 | 145 | 0.16 |
| | 25.15 | 3605 | 143 | 0.30 |

The foregoing experiments having shown satisfactorily that the streaming potential was independent of rate of flow or of the dimensions of the pores of the diaphragm, it appeared, in spite of the results of Table II (b), with a KCl solution in place of water, that a change in conductivity was being brought about when more, or less, pulp was packed into the diaphragm chamber. Cellulose, being a non-conductor of electricity, should, if it had any influence at all on the conductivity through the diaphragm, decrease the conductivity because of the displacement of conducting liquid. However, the experimental evidence pointed toward the fact that when more cellulose

was added per unit of volume, the conductivity increased instead of decreasing, causing a lowering of the observed E. M. F. (H) instead of an increase, as might be expected. A simple experiment to find whether or not the presence of cellulose fibers in the water did increase its conductivity was made. A thin suspension of pulp in water was allowed to stand in a corked erlenmeyer for several hours to insure that an equilibrium was attained, should any salts be present in the pulp. Then a large conductivity cell was filled alternately with the water alone, and with the water containing pulp in suspension, and the specific conductivity taken. The results are as follows:

1. Light suspension of pulp—specific conductivity = 8.60×10^{-6} mhos
2. Water (nearly free from fibers) " " = 8.32×10^{-6} "
3. Somewhat heavier suspension of pulp—spec. cond. = 9.70×10^{-6} "
4. Water (entirely free of fibers)—" " = 8.20×10^{-6} "

These results removed any doubts as to the cause of the failure of H/P to remain constant. When such a great change in specific conductivity is indicated with such small amounts of fibers as could be sucked up into the conductivity cell, it can readily be understood that in the diaphragm, where the fibers are very tightly packed, the change in conductivity might be very large and readily account for the large discrepancy in the H/P values.

The new cell described under "Method" was now designed, the object being to measure the specific conductivity of the diaphragm (κ_d) upon which the streaming potential had been measured. Due to the fact that the area of cross section of the new cell was greater than that of the old cell, it was found necessary to pack the pulp more tightly into it in order to prevent H/P from varying with P. The values of H/P obtained with the new cell are therefore, correspondingly lower than those obtained with the old cell. It was thought that the factor $H\kappa_d/P$ would be a constant for different degrees of packing, where (κ_d) is the specific conductivity of the diaphragm as a whole. This value could be calculated from the value of the conductivity cell constant of the chamber (C) (Fig. 3), when a N/100 KCl solution was used to calibrate it, and the resistance across the diaphragm itself. We assumed that when the diaphragm material was packed into the compartment, the cell constant varied but little from the value obtained with N/100 KCl solution. The electrodes, which served as retainers for the cell contents were of gold heavy enough to withstand a good deal of pressure so that the dimensions of the cell would not change with the tightness of packing the pulp in it.

The results shown in Table V (a) seem to indicate that the value $H\kappa_d/P$ is a fair approximation to a constant for a sulfite pulp. The packing is progressively tighter from A to D; all cases are, however, packed with sufficient tightness so that H/P is a constant, with variation in pressure, for a given diaphragm.

This experiment was repeated with some quantitative filter paper (Schleicher and Schüll, No. 589). Table V (b) shows the results. The value $H\kappa_d/P$ is approximately constant for the different packings, but is different from that obtained for the electrolyzed sulfite pulp. Since this value

must be multiplied by a constant (1.0596×10^8) to obtain the ζ -potential, it appeared that ζ varied with the kind or history of the cellulose.

TABLE V

A More Constant Value for the ζ -Potential obtained when Specific Conductivity of Diaphragm (κ_D) is used in Place of Specific Conductivity of Liquid in Bulk in the Streaming Potential Formula

| (a) For a Sample of Sulfito Pulp | | | | | |
|--------------------------------------------|----------|------|------|-----------------------|----------------------------------|
| | P | H | H/P | $\kappa_D \cdot 10^6$ | $\frac{H\kappa_D \cdot 10^6}{P}$ |
| | (cm.Hg.) | (mv) | | (mho) | |
| A | 55.0 | 48.0 | .872 | 2.51 | 2.19 |
| | 41.2 | 37.0 | .92 | 2.53 | 2.31 |
| | 26.2 | 24.5 | .935 | 2.53 | 2.36 |
| | 23.0 | 21.0 | .913 | 2.59 | 2.36 |
| B | 32.6 | 30.0 | .92 | 2.52 | 2.32 |
| | 44.1 | 40.5 | .92 | 2.52 | 2.32 |
| | 24.0 | 19 | .794 | 2.81 | 2.23 |
| C | 35.6 | 29 | .814 | 2.75 | 2.24 |
| | 49.7 | 41 | .824 | 2.70 | 2.23 |
| | 51.4 | 39.5 | .77 | 2.90 | 2.23 |
| D | 39.3 | 29.5 | .75 | 2.90 | 2.18 |
| | 27.7 | 21.0 | .76 | 2.90 | 2.20 |
| (b) For a Sample of S. and S. Filter Paper | | | | | |
| | P | H | H/P | $\kappa_D \cdot 10^6$ | $\frac{H\kappa_D \cdot 10^6}{P}$ |
| | (cm.Hg.) | (mv) | | (mho) | |
| A | 31.6 | 345 | 10.9 | 6.0 | 6.52 |
| | 22.96 | 253 | 11.0 | 5.8 | 6.46 |
| | 12.7 | 143 | 11.1 | 5.7 | 6.30 |
| | 18.4 | 200 | 10.9 | 5.8 | 6.36 |
| B | 14.9 | 159 | 10.7 | 6.3 | 6.7 |
| | 20.2 | 213 | 10.6 | 6.3 | 6.7 |
| | 27.3 | 281 | 10.3 | 6.3 | 6.5 |

These results indicated a sufficient constancy in the value $H\kappa_D/P$ to warrant its use in comparing celluloses from various sources in order to find to what extent they might vary. Measurements were, therefore, made upon several dialyzed pulps and upon cotton, with the result that the values of $H\kappa_D/P$ all lay between the values given by the sulfito pulp shown in Table V (a) and the S. and S. filter paper of Table V (b). However, results on these samples of pulp seemed to cast doubt upon the constancy of this value for any given pulp when the tightness of packing was varied. Table VI shows this for a dialyzed short fiber pulp.

TABLE VI
Evidence that Specific Conductivity of Diaphragm is not the Correct Value to use in the Streaming Potential Formula for Calculation of ζ -Potential

| P | H | H/P | $\kappa_D \cdot 10^6$ | $\frac{H\kappa_D \cdot 10^6}{P}$ |
|---------------|-------|------|-----------------------|----------------------------------|
| (cm.Hg.) | (mv) | | (mho) | |
| 28.0 | 100.0 | 3.66 | 1.80 | 6.5 |
| 17.0 | 69.0 | 4.05 | 1.60 | 6.5 |
| 14.8 | 53.6 | 3.62 | 1.56 | 5.6 |
| 10.0 | 36.7 | 3.67 | 1.50 | 5.9 |
| Tighter pack— | | | | |
| 16.1 | 36 | 2.24 | 1.76 | 3.96 |
| 29.1 | 65 | 2.23 | 1.74 | 3.89 |

This difference might be explained by the fact that this sample of pulp still contained some soluble ions, and these were leaching out into the solution. In this case, the concentration of electrolyte would be lower in the less tightly packed diaphragm than in the more tightly packed diaphragm, due to a faster rate of flow. Then, if the ζ -potential were an inverse function of this ion concentration, it might be expected that it would be higher where the ion concentration was low. But while this is a possible explanation, further study of the derivation of the streaming potential formula showed that a discrepancy might be expected when the specific conductivity of the diaphragm (κ_D) was used in the equation in place of the specific conductivity of the liquid (κ_s) as it exists in the diaphragm. The specific conductivity of the diaphragm (κ_D) would give a value for ζ , which would more closely approximate the true value than if the specific conductivity of the liquid in bulk (κ_L) were used, as it could be when glass tubes were employed as the diaphragm. But the real value which should be used for the specific conductivity is that of the liquid (κ_s) as it exists in the diaphragm.

The increase in specific conductivity of the liquid when the fibers are placed in the cell is due to a "surface conductance" along the surface of the fibers. By measuring the "cell constant" of the diaphragm after the streaming potential measurements have been made, and from measurements of the resistance across the diaphragm simultaneously with the streaming potential measurements, it is possible to find this specific conductivity of the liquid (κ_s) in the pores.

The "cell constants" of the diaphragms used in calculating the specific conductivity of the liquid in the diaphragm (i.e. κ_s) were obtained by the use of N/10 KCl solution as the standard conducting liquid. It was assumed that at that concentration of electrolyte the surface conductance would be negligible. In order to determine to just what extent this assumption was correct, the following experiment was carried out.

If the surface conductivity with N/10 KCl was, indeed, negligible, a series of "cell constants" made on the diaphragm with solutions of KCl of lower normality should approach the "cell constant" obtained with N/10 KCl as a

limit, and the concentration, "cell constant" curve should show no indications of attaining a higher value with increase in concentration of the standardizing solution. A series of apparent "cell constants" were determined on diaphragms "B," in Table VIII (a), and "B" in Table VIII (b), using solutions of KCl ranging from N/1000 to N/10, the specific conductivities of which were measured at the same temperature as that of the diaphragm.* Table VII shows how the apparent "cell constant" varied due to surface conductance. The same values are shown graphically in Fig. 2.

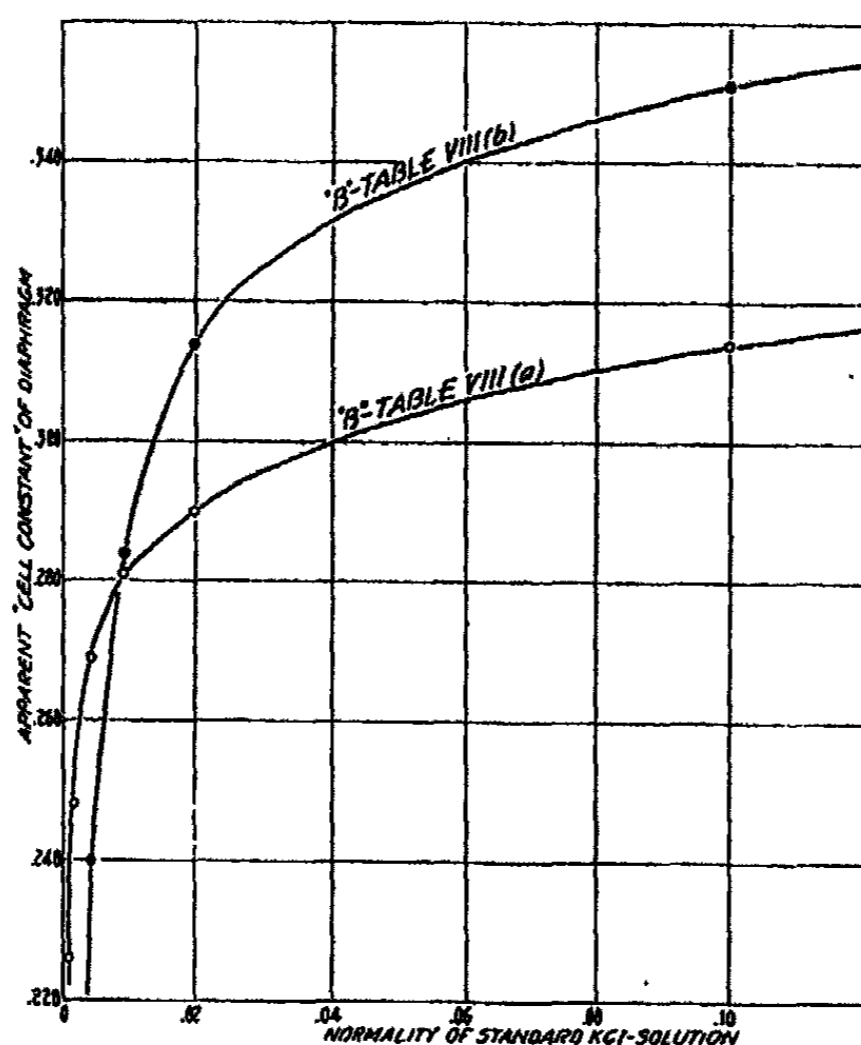


FIG. 2

Showing the Apparent "Cell Constant" of Diaphragms of Two Samples of Cellulose—Determined with KCl Solutions of Various Normalities as Standard Conducting Solutions.

TABLE VII

Variation of "Cell Constant" of Diaphragm with Specific Conductivity of Standardizing Solution

| KCl solution | "cell constants" —B (a) | —B (b) |
|--------------|-------------------------|--------|
| N/10 | .314 | .353 |
| N/50 | .290 | .314 |
| N/100 | .281 | .284 |
| N/200 | .274 | .245 |
| N/500 | .248 | .179 |
| N/1000 | .226 | .136 |

* All measurements were made in air at room temperature, 24°C, so that a small experimental error, due to temperature fluctuations of $\pm 1^\circ\text{C}$., will be present in all conductivity measurements made in this work. In most cases this error is of no great importance.

Attempts to obtain a mathematical expression for the curves given in Fig. 2 show that these curves are hyperbolas and may be expressed in equations of the form $-x/y = a + bx$. The following data indicate how closely an equation may be approximated. N = normality, C_o = "cell constant," C_c = "cell constant" calculated from the equation, and Δ the difference between C_o and C_c .

For curve (a) B—

| N | C_o | N/ C_o | C_c | Δ |
|-------|-------|----------|--------------------------------|----------|
| 0.100 | 0.314 | 0.31850 | 0.309 | -0.005 |
| 0.020 | 0.290 | 0.06900 | 0.301 | +0.011 |
| 0.010 | 0.281 | 0.03600 | 0.293 | +0.012 |
| 0.005 | 0.274 | 0.01825 | 0.278 | +0.004 |
| 0.002 | 0.248 | 0.00806 | 0.241 | -0.007 |
| 0.001 | 0.226 | 0.00442 | 0.227 | +0.001 |
| | | | $\sigma\Delta \div 6 = 0.0066$ | |

$$C_o = \frac{N}{0.00188 + 3.218 N}$$

From this equation C_o approaches the value 0.310 ± 0.0066 as a limit.

For curve (b) B—

| N | C_o | N/ C_o | C_c | Δ |
|-------|-------|----------|-------------------------------|----------|
| 0.100 | 0.353 | 0.2850 | 0.347 | -0.004 |
| 0.020 | 0.314 | 0.0636 | 0.322 | +0.008 |
| 0.010 | 0.284 | 0.0352 | 0.296 | +0.012 |
| 0.005 | 0.245 | 0.0204 | 0.255 | +0.010 |
| 0.002 | 0.179 | 0.0112 | 0.179 | 0.000 |
| 0.001 | 0.136 | 0.00735 | 0.120 | -0.016 |
| | | | $\Sigma\Delta \div 6 = 0.008$ | |

$$C_o = \frac{N}{0.00551 + 2.825 N}$$

For this equation C_o approaches the value 0.355 ± 0.008 as a limit.

In the case of curve (a) B [Table VII] plotted from data obtained with S. and S. filter paper, the "cell constant" obtained with N/10 KCl may be taken as the true value, while with curve (b) B made with the sulfite pulp, the surface conductance of the pulp still plays a small rôle even in concentrations of that normality.

When the specific conductivity of the water in "bulk" (κ_b) was compared with the specific conductivity of this same water as it exists in the diaphragm (κ_d), it was found that in diaphragms of the sulfite pulp the conductivity of the water increased in the order of 35 to 65 times the bulk conductivity, while with the S. and S. filter paper pulp it was only 8 to 11 times as great, depending, of course, on the concentration of the pulp in the diaphragm.

The conclusion arrived at from this experiment is that the "cell constant" of a diaphragm, showing a high surface conductance effect, cannot be safely assumed to be that obtained with N/10 KCl as the standard solution and that a more concentrated electrolyte must be used in the determination; but

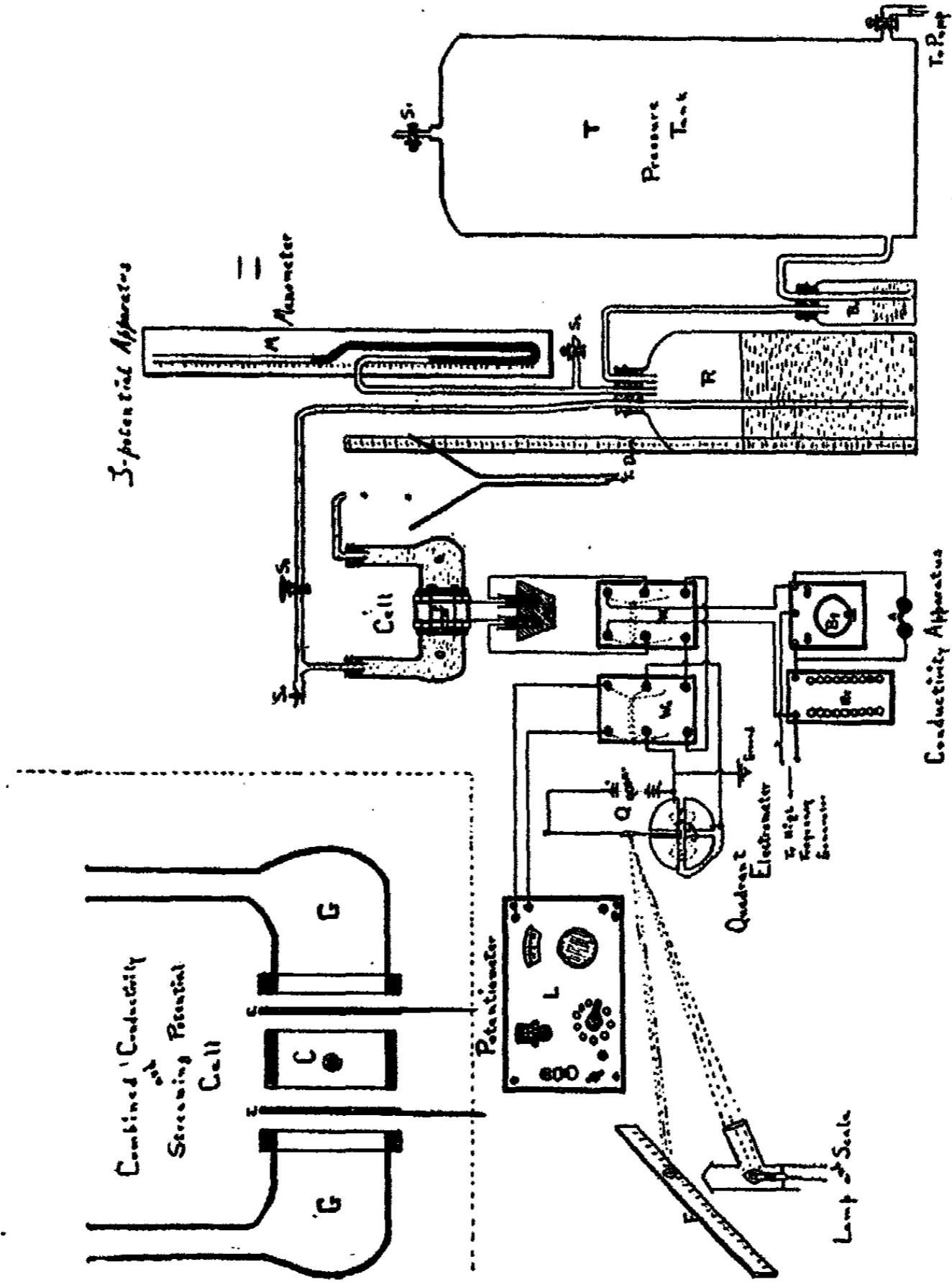


FIG. 3

with those diaphragms, having a relatively low surface conductance effect, the "cell constant" determined with N/10 KCl may be taken as the correct value.

Method

In Fig. 3 will be seen a diagram of the apparatus assemblage used for the determination of the ζ -potential on cellulose, or similar materials, by means of the streaming potential method. In order to calculate ζ from the equation

$$\zeta = \frac{4\pi\eta\kappa H}{Pe},$$
 it is necessary to measure three variables simultaneously,

that is, (1) the hydrostatic pressure (P), (2) the electromotive force (H) set up across the diaphragm, and (3) the conductivity (κ) of the liquid within the diaphragm.

As a source of pressure, a tank (T) of about 50 liters capacity was used. Air was pumped into this tank until the desired pressure was attained. This air was passed through washing bottle (Bo) and into the reservoir (R) which contained the liquid which was being forced through the diaphragm. Pressure on the surface of the liquid in (R) was measured with the mercury manometer (M). To obtain the value for the pressure (P) on the diaphragm, the pressure, due to the water column between the surface of the liquid in (R) and the point of emission of the liquid from the cell, had to be subtracted from the manometer reading. Stopcocks, S_1 and S_2 , were used to release the pressure from the tank and the reservoir, respectively. Stopcock, S_3 , could be used to stop the flow of the liquid through the cell when desired. S_4 was needed to allow air to escape from the first chamber of the cell when this was being filled with liquid.

The cell which is used, is a combination conductivity cell and streaming potential cell. It consists of a glass center compartment (C) into which the diaphragm material is packed, two perforated gold electrodes (E), and two glass end compartments (G) with heavy glass flanges fitting up against the electrodes and which serve as supports for a clamp which holds the whole cell tightly together. In order to make the cell water tight, thin rubber washers cut from dental dam rubber are placed between the electrodes and the glass, care being taken that these do not cover any of the surface of the electrode which should be exposed to the contents of the chamber (C). The electrodes are disks made of 14 K gold, one millimeter thick and 45 millimeters in diameter. The portion of the electrode which is exposed to the center compartment (C) is perforated with one millimeter holes as thickly as possible without lowering its strength.

At a point on the circumference of each gold disk is soldered a platinum wire which will dip into mercury cups (MC) and from which contact will be made with the electrical measuring equipment. Facility with which measurements could be made was increased by the use of two six-point double-throw switches (W_1 and W_2). To insure perfect contact in the switches,

mercury cups and copper rockers were used. With switch (W_1) the cell could be connected either with the conductivity apparatus or the potentiometric apparatus.

Early in the research it was found that the ordinary potentiometer could not be used for measuring the streaming potentials in such a cell as described, because of polarization of the electrodes due to passage of current through them while the null point was being sought. Attempts were made to use liquid contacts and non-polarizing electrodes (calomel half-cells) with the potentiometer, but the added resistance to the circuit was so great as to prevent any deflection of the galvanometer or even of the capillary electrometer, which is much more sensitive than most galvanometers. It will be remembered that Harrison (*loc. cit.*) had similar trouble, and overcame it by using a condenser and ballistic galvanometer. In the present work, a quadrant electrometer (Q) was used. This instrument is a capacity potentiometer and requires an almost infinitesimal amount of electricity flowing from the electrodes to charge it. With it, the polarization trouble was always either reduced to a constant factor or totally eliminated.

Switch (W_2) is wired to connect the quadrant electrometer either to the streaming potential cell or to a Leeds and Northrup Portable Potentiometer (L) which served as a calibrating instrument. The deflection on scale (F) of the light reflected from the mirror attached to the needle of the quadrant electrometer could be calibrated with the L. and N. Potentiometer and compared with readings taken from the streaming potential cell. The fiber used during the present measurements had a sensitivity of 125 mm. per 100 millivolts, at a scale distance of 1 meter. This made it possible to read potentials to an accuracy of approximately one millivolt.

The conductivity of the liquid in the diaphragm was measured with the aid of a ten meter bridge (B), ear phones (A), and high resistances (R_0). The cell constant in the absence of diaphragm material was measured with N/100 KCl and found to be 0.146. The cell was reassembled several times and its conductivity constant remeasured. There was a very small variation in this value. This value of cell constant, however, is not of such great importance. As will be seen later, any variation in the cell due to difference in assembling is eliminated when the measurement of the "cell constant" of the diaphragm is made. The important point to be noted now is the fact that resistance measurements across the diaphragm may be made easily at any time. Most of the early measurements given in the present paper were made without actually determining the "cell constant" of the diaphragm. In these measurements the specific conductivity of the diaphragm (κ_p) as a whole was taken, and the value for the cell constant of the chamber (C), that is, 0.146, was used. The value $H\kappa_p/P$ appeared to be a fairly close approximation to a constant, at any rate, this factor is much nearer constant (for different tightnesses of packing) than the factor (H/P) which Krzyt and Freundlich (*loc. cit.*) found to be constant for glass tubes. However, it was later shown that there is a factor $H\kappa_s/P$ where (κ_s) is the specific conductivity of the liquid in the diaphragm determined in the following manner, which is more nearly a

constant value under very great difference in tightness of packing (and therefore, difference in dimensions of the capillaries in the diaphragm) than is $H\kappa_0/P$. In all future work the value (κ_0) will be used. When it is used the values for ζ become absolute, in so far as certain fundamental assumptions discussed above will allow.

The value (κ_0) is determined by measuring the resistance across the diaphragm while the liquid, against which the ζ -potential is desired, is in the diaphragm pores. Then after all streaming potential measurements are completed upon the sample, the "cell constant" of the diaphragm is obtained by replacing all liquid in the diaphragm with N/10 KCl (or a more concentrated soln., if needed), measuring the resistance across it and calculating the cell constant in the usual manner for any conductivity cell. Then from the measurements of resistance obtained while the experimental liquid was present, and the new "cell constant," the specific conductivity (κ_0) of this liquid may be calculated. Care must be taken to use a standard solution of KCl (or other electrolyte) which is of sufficient strength to eliminate all surface conductance effects from the diaphragm, when it is present, in order that the value of the "cell constant" may be correct.

From the values of (P), (H), and (κ_0) thus obtained, ζ may be calculated. The coefficient of viscosity (η) is taken as equal to 0.01. (ϵ), the dielectric constant of water, has been considered as having the value 80. (P), which is observed in centimeters of mercury, must be expressed in absolute units, that is, in dynes. This is obtained by multiplying the cm. Hg. observed by the specific gravity of mercury, 13.6, and the force of gravity in dynes acting on one gram, i.e., 981. (H), observed in millivolts, must be divided by 1000 to reduce it to volts and by 299.86 to reduce volts to c. g. s. electrostatic units. (1 c. g. s. electrostatic unit = 299.86 absolute volts.) (κ_0), observed in ohms⁻¹ must be multiplied by 9×10^{11} to convert it into c. g. s. electrostatic units. (1 c. g. s. electrostatic unit = 9×10^{11} absolute ohm-cms.) The value of ζ obtained would be in electrostatic units. In order to obtain this value in volts, it must be multiplied by 299.86.⁶⁸

Then

$$\zeta = \frac{H\kappa_0}{P} \times \frac{9 \times 10^{11} \times 4 \times 3.1416 \times .01 \times 299.86}{13.6 \times 981 \times 10^3 \times 299.86 \times 80}$$

$$= 1.0596 \times 10^3 \times \frac{H\kappa_0}{P}$$

Where (ζ) is expressed in volts, (H) in millivolts, (κ_0) in reciprocal ohms and (P) in centimeters of mercury.

Results and Discussion

Results shown in Table VIII, (a), (b), and (c), serve to illustrate how constant the value $H\kappa_0/P$ has been found to be for three samples of paper pulp. Table VIII, (a) and (c), were obtained with samples of a quantitative filter paper (S. and S. No. 589). These two samples of filter paper were secured from the distributing firm at different times and were not of the same

⁶⁸ See International Critical Tables, 1, 27 (1926).

batch of paper. For Table VIII, (b), the diaphragms were made of the electrolyzed sulfite spruce pulp used throughout the development of the method. To insure uniformity of the pulp used in each series of diaphragms, these were prepared from a stock suspension of the pulp in water.

Fairbrother and Varley⁴⁴ have shown by electrosmosis experiments that sintered glass powder becomes hydrated on standing several days in contact with pure water and that the ζ -potential decreases as hydration increases, and it may become positively charged with solutions against which it formerly showed a negative charge. A similar phenomenon is noted with cellulose. If a dry sample of cellulose is allowed to stand a few days with water, a marked decrease in ζ -potential from the value given on the newly wetted pulp is observed. This decrease in ζ -potential approaches a limit with time and after a week the relative change per day is small. However, if the cellulose is placed in a ball-mill and beaten for a while, the ζ -potential again decreases and the decrease seems proportional to the degree of beating. Hydration seems therefore to decrease the ζ -potential on widely varied substances. The explanation probably lies in the variation in the fraction of the e -potential which is extant between the fixed and movable layers of the liquid, the hydrated layer forcing the fixed-movable interface further into the liquid.

In Series (a) a comparison is made between $H \cdot \kappa_p/P$ and $H \cdot \kappa_s/P$. The "cell constants" of the diaphragms which were used in the calculation of κ_s were determined with N/10 KCl as the standard conductivity solution. The cell constant used in calculating κ_p was that of the cell assembled with no pulp in it, which had the value, as mentioned before, of 0.146.

The dry weights of the diaphragms are given in Series (b) and (c) to indicate the relative tightness of pack of the diaphragms. The volume occupied being equal in every case, the tightness of pack is directly proportional to the weight of the diaphragm. In Series (c) the specific conductivity of the distilled water in bulk is given for each diaphragm. This value, (κ_d), when compared with (κ_s) shows that the specific conductivity of the water is increased from 9 to 10 times when it is in the diaphragm of S. and S. filter paper pulp. Though the bulk specific conductivity of the distilled water was not measured for Series (b) it may be considered of the same order of magnitude as that used in Series (c), in which case it will be seen that in contact with the sulfite pulp the specific conductivity of the water is increased 35 to 65 times, depending upon the size of the pores in the diaphragm. The "cell constants" used in calculating κ_s for diaphragms of Series (b) were measured with N/5 KCl instead of N/10, due to the fact that, in cases where the surface conductance is so high, this effect is still noticeable even when N/10 KCl is present as the liquid in the interstices of the diaphragm.

Values of the ζ -potential for the two samples of S. and S. filter paper (rag pulp) and for the sulfite pulp (wood pulp) are 0.0214 volts, 0.0161 volts, and 0.0083 volts, respectively. The ζ -potential on a sample of cellulose is a

⁴⁴ Fairbrother and Varley: J. Chem. Soc., 1927, 1584.

function of both its origin and history, the latter probably being the more important of the two.

These results indicate that, while the ζ -potential on cellulose is a variable from sample to sample, it can be determined accurately by the streaming potential method, provided a proper value for the conductivity (κ) in the streaming potential equation is obtained. This conclusion carries with it the corollary that the assumptions upon which the streaming potential equation is based are accurate and true within experimental error.

It is absolutely necessary in making ζ -potential measurements on cellulose and like colloids that foreign ions shall be absent. Traces of such ions, especially the polyvalent positive ions, will cause great variations in the ζ -potential. The accompanying Fig. 4 shows this effect with a series of chlorides of various positive ions (H, K, Mg, La, and Al) upon the value $H\kappa_D/P$ on diaphragms made from the S. and S. filter paper. These curves serve to illustrate one application of the method for measuring ζ given in this paper, that is, the study of ion effects upon colloids. These effects have

TABLE VIII (a)
Comparison of $H\kappa_D/P$ and $H\kappa_S/P$ for Various Diaphragms of a Sample of S. and S. Filter Paper

| P (cm. Hg.) | H (mv) | H/P | $\kappa_D \cdot 10^6$ (mho) | $\kappa_S \cdot 10^6$ (mho) | $\frac{H\kappa_D \cdot 10^6}{P}$ | $\frac{H\kappa_S \cdot 10^6}{P}$ | Cell Constant for κ_S |
|----------------|-----------|------|--------------------------------|--------------------------------|----------------------------------|----------------------------------|------------------------------------|
| 5.8 | 104 | 17.9 | 5.75 | 11.7 | 10.30 | 20.9 | A |
| 12.9 | 220 | 17.1 | 5.74 | 11.6 | 9.70 | 19.8 | 0.297 |
| 15.1 | 253 | 16.8 | 5.42 | 11.4 | 9.20 | 19.1 | |
| 9.95 | 160 | 16.1 | 5.87 | 12.6 | 9.4 | 20.3 | B |
| 14.9 | 239 | 16.0 | 5.87 | 12.6 | 9.2 | 20.2 | 0.314 |
| 12.9 | 214 | 16.5 | 5.87 | 12.6 | 9.7 | 20.9 | |
| 10.3 | 150 | 14.5 | 6.39 | 14.65 | 9.3 | 21.3 | C |
| 18.4 | 276 | 14.9 | 6.10 | 14.0 | 9.1 | 20.8 | 0.335 |
| 14.45 | 216 | 14.9 | 6.10 | 14.0 | 9.1 | 20.9 | |
| 10.2 | 153 | 14.8 | 6.10 | 14.0 | 9.0 | 20.8 | |
| 11.8 | 140 | 11.9 | 6.84 | 16.7 | 8.1 | 19.7 | D |
| 17.2 | 205 | 11.9 | 6.84 | 16.7 | 8.1 | 19.7 | 0.354 |
| 20.7 | 247 | 11.9 | 6.84 | 16.7 | 8.1 | 19.7 | |
| 16.9 | 195 | 11.4 | 6.37 | 15.9 | 7.26 | 19.1 | E |
| 22.5 | 264 | 11.7 | 6.32 | 15.8 | 7.40 | 19.6 | 0.385 |
| 24.2 | 293 | 12.1 | 6.32 | 15.8 | 7.60 | 20.3 | |

Ave. = 20.2

$$\zeta = 20.2 \times 10^{-6} \times 1.0596 \times 10^2 = .0214 \text{ volts.}$$

TABLE VIII (b)
 Values of $H\kappa_s/P$ for Diaphragms of Widely Varying Densities Are Constant for a Sample of Sulfite Pulp

| P (cm.Hg.) | H (mv) | H/P | $\kappa_s \cdot 10^4$ (mho) | $\frac{H\kappa_s \cdot 10^4}{P}$ (mho) | Cell Constant for κ_s | Dry Wt. Diaphragm (gm.) | |
|---------------|-----------|------|--------------------------------|-------------------------------------------|---------------------------------|-------------------------------|---|
| 16.15 | 25.7 | 1.59 | | | | | |
| 27.40 | 42.5 | 1.56 | | | | | |
| 36.80 | 59.4 | 1.61 | | | | | |
| 22.85 | 36.9 | 1.61 | | | | | A |
| | Average | 1.59 | 4.94 | 7.86 | .310 | — | |
| 13.8 | 9.6 | .695 | | | | | |
| 23.7 | 16.4 | .692 | | | | | |
| 34.3 | 23.6 | .686 | | | | | |
| 46.7 | 31.8 | .680 | | | | | |
| 36.4 | 25.1 | .690 | | | | | |
| 15.8 | 11.0 | .696 | | | | | B |
| | Average | .688 | 10.8 | 7.43 | .353 | 5.037 | |
| 14.6 | 18.0 | 1.23 | | | | | |
| 23.7 | 28.5 | 1.20 | | | | | |
| 32.6 | 40.5 | 1.24 | | | | | |
| 24.2 | 31.2 | 1.29 | | | | | |
| 14.1 | 19.7 | 1.39 | | | | | |
| 25.8 | 35.3 | 1.37 | | | | | |
| 37.3 | 48.6 | 1.30 | | | | | C |
| | Average | 1.29 | 5.68 | 7.33 | .313 | 4.190 | |
| 14.0 | 17.8 | 1.27 | | | | | |
| 23.2 | 30.1 | 1.29 | | | | | |
| 34.3 | 46.6 | 1.36 | | | | | |
| 23.9 | 33.8 | 1.41 | | | | | |
| 15.5 | 22.8 | 1.47 | | | | | D |
| | Average | 1.38 | 5.80 | 8.01 | .321 | 4.237 | |
| 14.4 | 9.6 | .666 | | | | | |
| 24.9 | 16.3 | .656 | | | | | |
| 37.7 | 25.9 | .687 | | | | | |
| 47.7 | 31.1 | .651 | | | | | |
| 42.4 | 28.4 | .669 | | | | | |
| 30.9 | 21.2 | .686 | | | | | E |
| | Average | .669 | 11.6 | 7.76 | .375 | 5.426 | |
| | Average | | | 7.68 | | | |

$$\xi = 7.68 \times 10^{-5} \times 1.0596 \times 10^2 = .0083 \text{ volts.}$$

TABLE VIII (c)

Values of $H\kappa_s/P$ for Diaphragms of Varying Densities Are Constant for a Sample of S. and S. Filter Paper

| P (cm.Hg.) | H (mv) | H/P | $\kappa_s \cdot 10^6$ (mho) | $\frac{H\kappa_s \cdot 10^6}{P}$ (mho) | Cell Con- stant for κ_s | Dry Wt. "Bulk" Diaphragm (gm.) | $\kappa_L \cdot 10^6$ |
|---------------|-----------|-------|--------------------------------|-------------------------------------------|--------------------------------------|--------------------------------------|-----------------------|
| 40.60 | 311 | 7.68 | | | | | |
| 32.40 | 251 | 7.75 | | | | | |
| 22.50 | 177 | 7.87 | | | | | |
| 21.40 | 169 | 7.90 | | | | | |
| 14.30 | 113 | 7.90 | | | | | A |
| | Average | 7.82 | 19.20 | 15.00 | .394 | 6.81 | 1.81 |
| 30.10 | 296 | 9.85 | | | | | |
| 23.90 | 237 | 9.92 | | | | | |
| 21.50 | 214 | 9.96 | | | | | |
| 15.20 | 160 | 10.50 | | | | | |
| 10.08 | 106 | 10.50 | | | | | B |
| | Average | 10.14 | 15.02 | 15.23 | .370 | 6.36 | 1.62 |
| 29.17 | 297 | 10.17 | | | | | |
| 23.81 | 247 | 10.35 | | | | | |
| 19.52 | 203 | 10.41 | | | | | |
| 13.85 | 144 | 10.40 | | | | | |
| 29.97 | 304 | 10.16 | | | | | |
| 24.37 | 250 | 10.25 | | | | | |
| 18.56 | 192 | 10.33 | | | | | C |
| | Average | 10.31 | 15.22 | 15.70 | .375 | 6.44 | 1.75 |
| 39.50 | 313 | 7.92 | | | | | |
| 32.57 | 259 | 7.95 | | | | | |
| 24.28 | 198 | 8.16 | | | | | |
| 18.65 | 156 | 8.36 | | | | | |
| 31.90 | 254 | 7.96 | | | | | |
| 24.41 | 197 | 8.07 | | | | | D |
| | Average | 8.07 | 18.62 | 15.05 | .393 | 6.86 | 1.67 |
| | Average | | | 15.24 | | | |

$$\zeta = 15.24 \times 10^{-5} \times 1.0596 \times 10^2 = .0161 \text{ volts.}$$

already been studied extensively by various methods, cataphoresis, electros-mosis, adsorption values, precipitation effects, etc. The advantage of the present method lies in its ease of manipulation and, we believe, the absolute character of the values obtained.

No discussion of Figure 4 will be given in the present paper, other than to point out some of the more interesting features. It will be seen that the Al^{+++} ion brings the cellulose to the iso-electric point at a concentration of about 0.0007 N, while none of the others, except possibly the H^+ , showed indications of reversing the charge. The K^+ ion, in very dilute solutions appears to increase the potential, while later decreasing it. As mentioned before, this effect may be due to a large change in the dielectric constant in low concentrations without a corresponding decrease in ζ to neutralize the effect. It is conceivable that at low concentrations, mixtures of K^+ and other ions (Mg^{++} , Al^{+++}) might be found where there was no apparent change in (ζ). This would be a case of ion antagonism. With the H^+ ion, the curve shows a

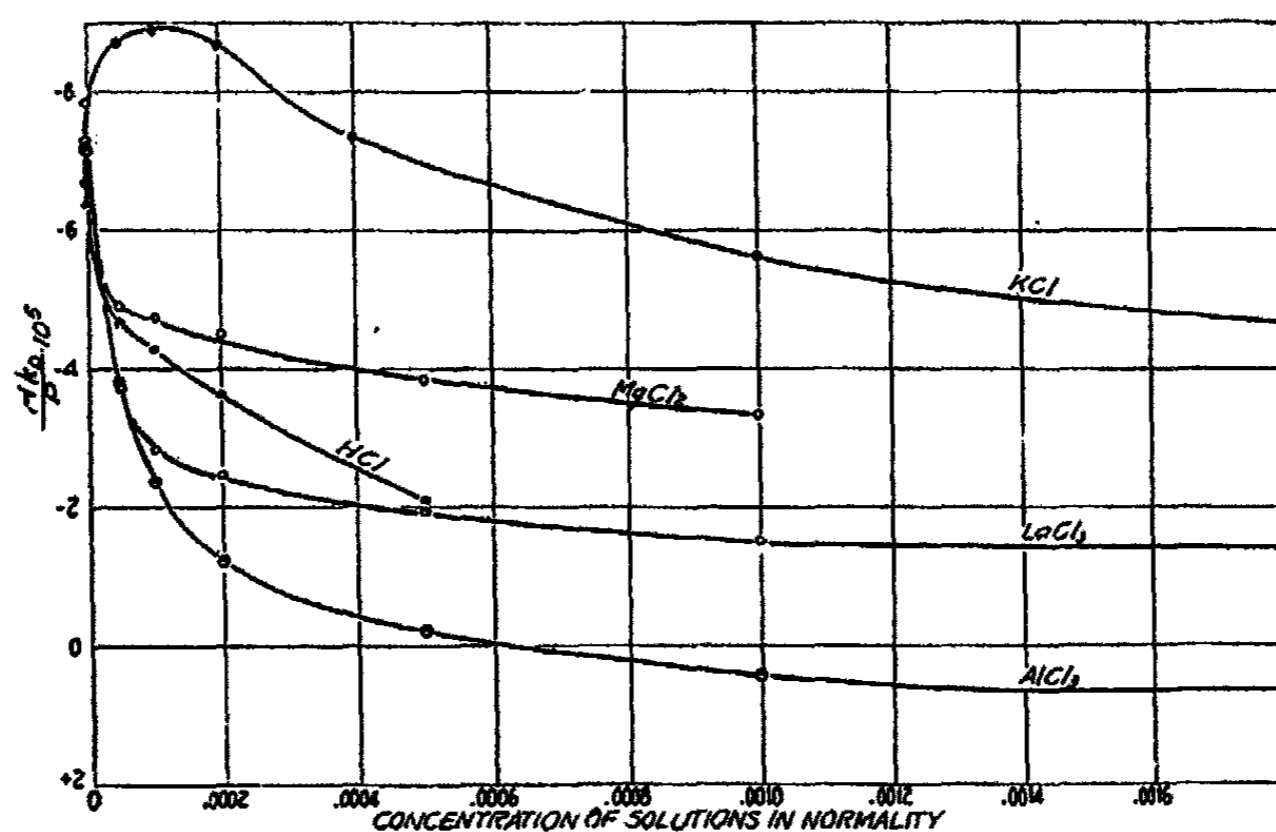


FIG. 4
Showing Ion Effects upon the ζ -Potential on Cellulose

decided tendency toward decreasing ζ up to a concentration of 0.0005 N, above which it was found impossible to make measurements, due to the enormous increase in surface conductance of the diaphragm when HCl was present. Al^{+++} and La^{+++} both definitely decreased the surface conductance of the pulp. This effect will also be studied more in detail later. The limiting factor in this method for studying ion effects is the conductivity. When this factor becomes too great, no measurements can be made. However, due to the fact that ion effects are usually those of extremely dilute solutions, this limitation is in most cases not of very great importance.

Summary

A method for the determination of ζ -potentials on colloid materials of such nature as cellulose, by means of the "streaming potential" measurements, is described.

A review of the literature and development of the "streaming potential" equation, together with the assumptions contained therein, is given.

Considerations are offered which indicate that measurements of the specific conductivity of the liquid in the diaphragm, which may vary widely from that of the liquid in bulk, may be made with a high degree of accuracy. The values for ζ resulting from the use of this value for the specific conductivity in the "streaming potential" equation, are to be regarded as absolute (not simply comparative) in so far as the assumptions relative to the other functions in the equation will allow.

Results indicate that ζ varies with the source and history of a sample of cellulose. An approximate value of ζ for two samples of a rag pulp and for a wood pulp are given; these values are .0214, .0161, and .0083 volts, respectively.

Acknowledgment

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29-22

A PHYSICO-CHEMICAL STUDY OF GUM ARABIC*

BY ARTHUR W. THOMAS AND HARRY A. MURRAY, JR.

There is very little in recent literature concerning the chemistry of gum arabic other than some isolated experimental facts. The complexity of the chemical behavior of the gums is frequently referred to their colloidal nature, and hence left for the present at least, as being not capable of explanation. This investigation was undertaken with the hope of establishing some definite stoichiometrical relations in connection with the colloid-chemical behavior of purified gum arabic.

Gum arabic occurs in the vegetable kingdom as the exudate of the *Acacia Senegal*. It is classified¹ as a colloidal polysaccharide. Such diverse colloids as dextrans, glycogen, cellulose, starch, mucilages, inulin and the true gums are in the same classification since they possess the common property of yielding upon hydrolysis, one or more sugars, generally pentoses or hexoses. Gum arabic is a typical true gum, i.e. it dissolves in water to form a clear filterable solution. Upon hydrolysis with sulphuric acid it yields the pentose sugar, arabinose, and relatively smaller quantities of the hexose sugar, galactose. The hydrolysis with sulphuric acid, also yields the so-called arabic acid nucleus to which the residues of arabinose and galactose are considered to be attached.² The "arabic acid" is of variable composition. The specific rotatory power varies from over plus 80 to minus 80 according to the origin. Herzfeld obtained from a levorotatory arabic acid 15.3 percent furfural and 11.5 percent mucic acid, and from a dextrorotatory arabic acid, 5.9 percent furfural and 41.7 percent mucic acid, showing the acid to be a galactoaraban of varying composition. Neubauer assigns the formula $(C_{12}H_{22}O_{11})_n$ to arabic acid,³ while O'Sullivan⁴ gives it as $C_{39}H_{142}O_{74}$. Arabinose is the product of hydrolysis using both dilute and concentrated hydrochloric acid. The ash is reported to be about 3.5 percent, and is mainly calcium carbonate, with some potassium carbonate.⁵

A résumé, too extensive to include in this paper, of some qualitative tests for gum arabic and its quantitative determination are given in a Bureau of Standards Bulletin.⁵

The methods of purification may be roughly divided into two classes which in turn may be combined as was done in this investigation. The first depends upon the fact that gum arabic is insoluble in a solution containing more than 60 percent alcohol,⁶ and the second, that a membrane may be prepared to which the colloidal gum arabic is impermeable, and through which the mineral ions may pass. According to Graham, arabic acid containing but 0.1 percent of ash may be prepared in five days by dialyzing a 20 percent solution of the gum with 4 or 5 percent hydrochloric acid.⁷ O'Sullivan purified the gum by dissolving in water and adding two or three times as much hydrochloric acid

*Contribution from the Department of Chemistry, Columbia University, No. 560.

as was required to combine with the metals present. He repeated the procedure four times, washing free from chloride with alcohol. The specific rotary powers of the four precipitates ranged from -25.7 to -27.0 indicating a homogeneous product.

Materials and Method of Purification

The material used in this investigation was "gum arabic" obtained from a jobber from stock shipped from Port Sudan, and is therefore the kind known as Sudan gum. It was purified as follows. A 100 gram portion of the commercial gum was dissolved in 500 cc of water, containing 5 cc of 12N hydrochloric acid. This solution was stirred mechanically for one half hour, after which alcohol was added slowly and with constant stirring to complete precipitation. In such a case the precipitate was fine, it settled and filtered readily. The precipitate was then filtered off through linen using suction. This operation, i.e., solution in water acidified with hydrochloric acid, and subsequent precipitation with alcohol, was repeated four times. The material thus obtained was dissolved in water and electrodialed for 50 hours. The solution was adjusted to $\text{pH} = 5.0$ by means of ammonium hydroxide and the electro dialysis continued until there was no test for the tenacious chloride ion in the diffusate. This required between 50-100 hours additional electro dialysis.

The electro dialysis was carried out in a three-compartment wooden cell,⁸ each compartment having a capacity of about 1500 cc. The membranes consisting of a coating of collodion on linen were fastened between the sections by means of bolts and rubber gaskets. The E. M. F. employed was 240 volts, and the only resistance used was that of the solution itself. Plates of carbon about 12×12 cm were used as electrodes. The carbon anode disintegrated badly and formed a carbon hydrosol in the compartment, but this introduced no complication since the carbon did not pass through the collodion membrane. The difficulty of testing for chloride ion in the anode compartment was overcome by the use of a platinum electrode at such times as the test was desirable. At no time was the temperature in the electrode compartments allowed to rise above 40°C .

There was a trace of reducing sugar in the original gum, one gram yielding 6 milligrams of cuprous oxide by the method of Quisumbing and Thomas,⁹ but immediately after purification the arabic acid did not reduce Fehling solution. At the end of four weeks, the stock arabic acid solution reduced Fehling solution slightly. The amount of reducing sugar present was a negligible factor for the following reasons. Its removal did not affect the specific rotatory power of the gum arabic, for that property was identical before and after purification. Further the optical rotatory power of the stock solution did not change even on long standing. The criteria of purity were the negligible amount of ash, and the uniformity of the product though the method of purification (time of dialysis) was varied, (50-100 hours). The purified product thus obtained will be referred to in this paper as arabic acid.

Four separate batches were prepared for use in this work, i.e. as one supply was being depleted, another was in the process of purification. The data obtained using all four solutions were concordant and reproducible though the supply of a given solution would last as long as five weeks during an investigation.

A one percent solution of purified arabic acid showed a pH value of 2.70 which is equivalent to that of a 0.02N solution of hydrochloric acid. This seemed unusual and was deemed worthy of investigation. Both the commercial gum arabic and the purified arabic acid were analyzed for phosphorus and sulphur in the thought that the presence of these substances as phosphates or sulphates, either naturally or by hydrolysis would account for the acidity. Sulphur was not present as shown by fusion with sodium and subsequent application of the sodium nitroprusside and methylene blue tests.¹⁰ The negative results were confirmed by fusion with sodium carbonate and potassium nitrate with subsequent test for barium sulphate.¹¹ Hence gum arabic is not a sulfuric acid ester as agar-agar has been shown to be.¹²

The phosphorus content was determined by fusion with sodium carbonate and potassium nitrate and subsequent treatment with ammonium phosphomolybdate solution.^{11, 12} There is a trace of phosphorus, not more than one tenth of one percent and not enough to account for the acidity. Further the nature of the titration curve, given later indicates that the acidity cannot be due to an acid as weak as phosphoric acid. Matthews¹ says that gums "nearly always contain phosphoric acid, which it is impossible to get entirely separated from the organic matter without hydrolysis. The phosphoric acid appears to be in union with the gum molecule and it is not impossible that it plays a very important part in the synthesis of the gum." It was felt that if the gum did yield the phosphate anion in solution it would have been removed during the purification process. If it were not, its presence in the amount indicated could not account for the acidity.

Apparently the high-molecular-weight arabic acid, the gummy residue so resistant to hydrolysis, is a strong acid.

In Table I is given a summary and a comparison of analyses made upon the commercial and purified products.

TABLE I
Summary of Analyses

| | Commercial gum | Purified gum |
|----------------------------------------------------------|----------------------------------|----------------------------------|
| $[\alpha]_D^{25}$ — (one percent solution) | -24.30 | -24.30 |
| Ash (percent) | 2.78 | 0.08 |
| Dextrin | none | none |
| Reducing sugar (mgm Cu ₂ O from 1 gr. gum) | 6.5 | none |
| Nitrogen (percent) | 0.36 | 0.33 |
| Phosphorus | trace (less than 0.1 percent) | trace (less than 0.1 percent) |
| Chloride ion | none | none |
| Sulphur | none | none |

The purified arabic acid must be kept in solution, for the product on drying, either with alcohol or by heating (vacuum distillation) is rendered practically insoluble in water. The concentration of the stock solution was determined, and the samples used were taken from this stock solution.

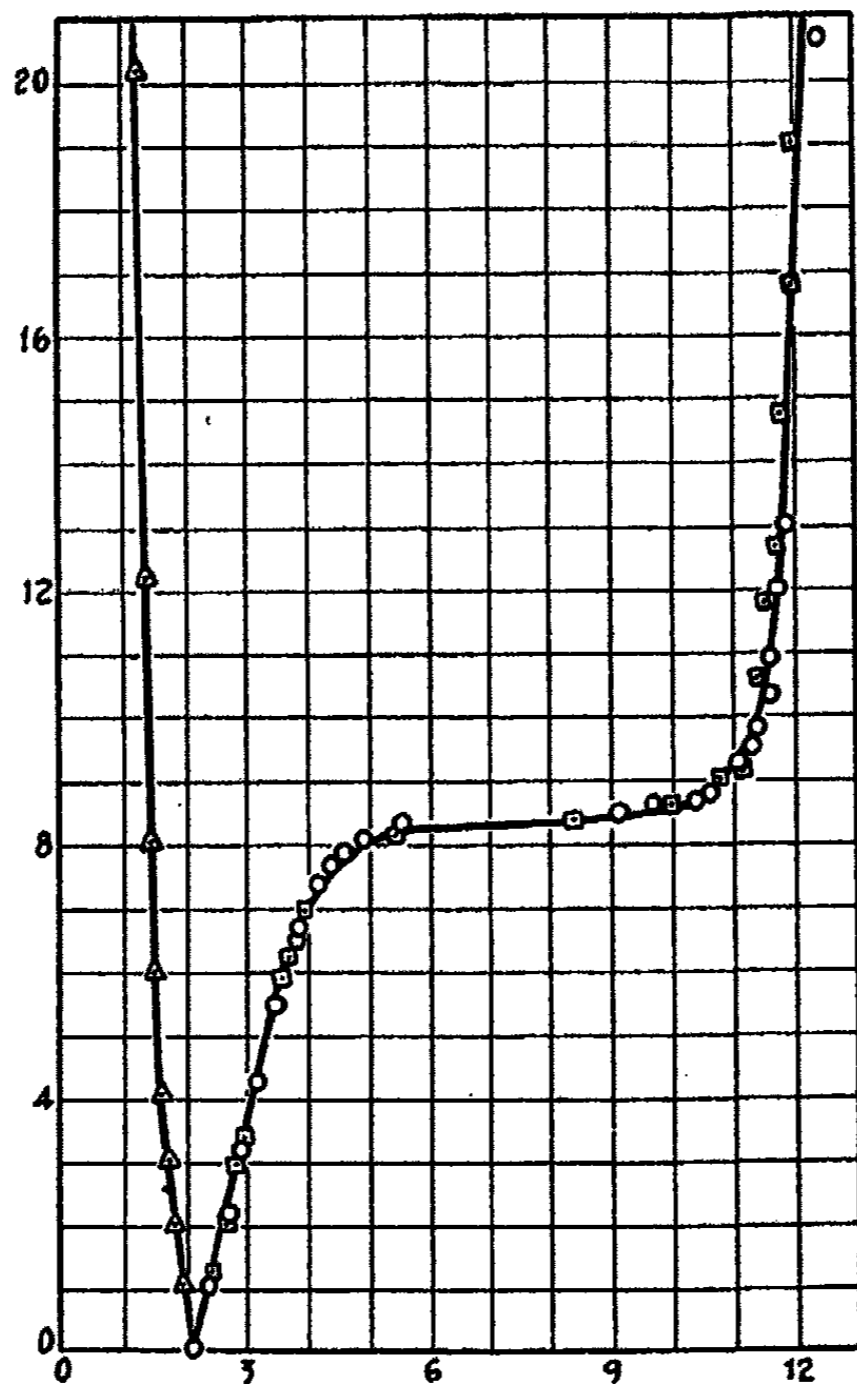


FIG. 1

Titration of arabic acid with acid and alkali.

$\Delta - \Delta = \text{HCl}$. $\circ - \circ = \text{NaOH}$. $\square - \square = \text{Ba}(\text{OH})_2$.

Abscissae = pH.

Ordinates = cubic centimeters of 0.1N base (or acid) added.

Titration with Acid and Base

Since this investigation was designed to extend a chemical viewpoint to the colloidal gum, the first step undertaken was to find out whether the substances formed true ionizable salts in the presence of acids and alkalis. A one gram

TABLE II
Titration of one gram of arabic acid* with 0.1N acid and alkali

| NaOH | | | | | |
|------------------------|----------------------|------|------------------------|----------------------|-------|
| 0.1N acid or alkali | Observed E. M. F. | pH | 0.1N acid or alkali | Observed E. M. F. | pH |
| 0.00 | 0.3742 | 2.15 | 8.49 | 0.7806 | 9.14 |
| 1.09 | 0.3894 | 2.41 | 8.60 | 0.8126 | 9.74 |
| 2.18 | 0.4067 | 2.71 | 8.70 | 0.8534 | 10.41 |
| 3.27 | 0.4215 | 2.96 | 8.82 | 0.8617 | 10.59 |
| 4.36 | 0.4359 | 3.21 | 9.03 | 0.8816 | 10.93 |
| 5.45 | 0.4523 | 3.50 | 9.25 | 0.8928 | 11.13 |
| 6.54 | 0.4707 | 3.82 | 9.46 | 0.9007 | 11.26 |
| 6.75 | 0.4733 | 3.86 | 9.79 | 0.9094 | 11.41 |
| 6.96 | 0.4776 | 3.94 | 10.34 | 0.9187 | 11.57 |
| 7.18 | 0.4838 | 4.05 | 10.88 | 0.9256 | 11.61 |
| 7.42 | 0.4922 | 4.19 | 11.97 | 0.9337 | 11.83 |
| 7.73 | 0.5037 | 4.39 | 13.06 | 0.9393 | 11.93 |
| 7.94 | 0.5183 | 4.64 | 27.20 | 0.9738 | 12.43 |
| 8.16 | 0.5357 | 4.94 | 38.08 | 0.9812 | 12.56 |
| 8.38 | 0.5726 | 5.58 | 54.40 | 0.9882 | 12.68 |
| Ba(OH) ₂ | | | | | |
| 0.1N acid or alkali | Observed E. M. F. | pH | 0.1N acid or alkali | Observed E. M. F. | pH |
| 0.00 | 0.3764 | 2.18 | 8.46 | 0.7416 | 8.44 |
| 0.85 | 0.3881 | 2.40 | 8.67 | 0.8322 | 9.98 |
| 1.27 | 0.3941 | 2.41 | 9.13 | 0.8974 | 11.17 |
| 2.12 | 0.4064 | 2.71 | 9.10 | 0.8796 | 10.79 |
| 2.96 | 0.4173 | 2.89 | 9.31 | 0.8899 | 10.97 |
| 3.39 | 0.4218 | 2.97 | 10.57 | 0.9147 | 11.39 |
| 4.23 | 0.4337 | 3.17 | 11.84 | 0.9257 | 11.55 |
| 5.50 | 0.4505 | 3.96 | 12.69 | 0.9317 | 11.68 |
| 5.92 | 0.4586 | 3.60 | 14.81 | 0.9372 | 11.78 |
| 6.35 | 0.4665 | 3.73 | 16.92 | 0.9456 | 11.89 |
| 6.98 | 0.4803 | 3.97 | 19.04 | 0.9502 | 12.00 |
| 7.61 | 0.5030 | 4.36 | 21.12 | 0.9527 | 12.03 |
| 8.25 | 0.5841 | 5.74 | | | |
| HCl | | | | | |
| 0.1N acid or alkali | Observed E. M. F. | pH | 0.1N acid or alkali | Observed E. M. F. | pH |
| 0.00 | 0.3745 | 2.17 | 8.10 | 0.3316 | 1.45 |
| 1.01 | 0.3622 | 1.97 | 12.16 | 0.3283 | 1.40 |
| 2.03 | 0.3536 | 1.82 | 20.26 | 0.3216 | 1.28 |
| 3.04 | 0.3472 | 1.71 | 30.39 | 0.3172 | 1.21 |
| 4.05 | 0.3424 | 1.63 | 40.52 | 0.3144 | 1.17 |
| 6.08 | 0.3359 | 1.52 | 50.65 | 0.3126 | 1.13 |

* The original volume was that volume of stock solution which contained one gram of the arabic acid, usually from 15 cc. to 20 cc.

portion of the purified arabic acid was titrated electrometrically* with 0.1N solutions of sodium hydroxide, barium hydroxide and hydrochloric acid. The data obtained are given in Table II and plotted in Fig. 1.

The curves for sodium and barium hydroxide are practically identical indicating that the arabic acid combines with alkali in equivalent proportions. The region of neutrality is between $\text{pH} = 5.0$ and $\text{pH} = 10.0$ and the end point (stoichiometric) indicates that 8.5cc of 0.1N alkali combine with one gram of acid. This result yields 1200 (1177) as the equivalent weight of the arabic acid. The sharp point of inflection on the curve bears out the conclusion that the acid is a strong one. The curve for hydrochloric acid suggests that the arabic acid is not amphoteric, a conclusion confirmed by further work reported later in this paper.

The Alkali-Binding Capacity of Arabic Acid

Introductory:—

The titration curves using sodium and barium hydroxides indicated that the arabic acid combined with bases according to the laws of primary valency, in brief as any simple inorganic acid and base combine. The next step taken to fix the simple stoichiometrical behavior of arabic acid was a measure of its base-combining capacity. No attempts were made here to determine an acid-combining capacity for preliminary studies in work to be described later clearly indicated that the arabic acid did not behave as a base. If it could be shown that one gram of arabic acid was capable of combining with a definite amount of alkali under different conditions, viz., varying concentrations of alkali, it was felt that our purpose to show the presence of true ionizable salts would be realized.

Procedure:—

The alkali-combining capacity was determined by a method similar to that described by Loeb¹⁴ and by Hoffman and Gortner.¹⁵

Varying normalities of sodium hydroxide were prepared in 25 cc volumetric flasks and the pH values determined potentiometrically. The data are given in Table III. The hydroxyl ion concentration was calculated from the observed pH using 1×10^{-14} as the dissociation constant for water. From these data a curve was plotted for subsequent calculations. This curve is not given here for economy of space.

A known weight of gum was placed in a 25 cc volumetric flask and the solution made up to a definite normality of sodium hydroxide by adding the same amount of standard alkali as before, that is when no acid is present. The pH value was determined, and the hydroxyl ion concentration calculated as above. By the ionization curve then, plotted from the data in Table III,

* The hydrogen ion concentrations of the equilibrium solutions in all the work in this paper were determined potentiometrically at room temperature. The hydrogen electrode used was the Hildebrand type as modified by Wilson.¹³ The calomel electrode used was of the type described by Wilson.¹³ Saturated potassium chloride (4.1N) was used and considered to eliminate liquid junction potentials. The potentiometer used was the portable hydrogen potentiometer (#7655) manufactured by the Leeds and Northrup Co., and said by them to have an accuracy of plus or minus 0.5 millivolts.

the equilibrium ion concentration obtaining in the sodium arabate solution can be changed into normality. The amount of base bound by the arabic acid in terms of normality was determined by the difference between the original normality (N) of the sodium hydroxide solution without the arabic acid, and the measured normality (N') of the sodium hydroxide solution containing the arabic acid, each having been made up to the same original normality. The amount of base bound by acid and designated by n is then equal to $N - N'$.

In this method of calculation it is necessary to assume that the same normality of alkali gives the same hydroxyl ion concentration whether arabate ion is present or not. The low concentration of arabate ion present would not in all probability materially affect the hydroxyl ion.

TABLE III
Potentiometric determination of hydrogen ion concentration with varying normalities of sodium hydroxide

| Normality | E.M.F. | pH | C_{OH^-} | Normality | E.M.F. | pH | C_{OH^-} |
|-----------|--------|-------|------------|-----------|--------|-------|------------|
| 0.0044 | 0.9267 | 11.57 | 0.00372 | 0.1502 | 1.0090 | 12.93 | 0.08511 |
| 0.0087 | 0.9432 | 11.83 | 0.00676 | 0.1670 | 1.0107 | 12.98 | 0.09550 |
| 0.0131 | 0.9533 | 11.99 | 0.00977 | 0.1879 | 1.0152 | 13.02 | 0.1050 |
| 0.0218 | 0.9671 | 12.21 | 0.01621 | 0.2297 | 1.0184 | 13.09 | 0.1230 |
| 0.0300 | 0.9738 | 12.37 | 0.02344 | 0.2427 | 1.0200 | 13.12 | 0.1318 |
| 0.0457 | 0.9827 | 12.50 | 0.03162 | 0.2506 | 1.0226 | 13.13 | 0.1349 |
| 0.0500 | 0.9846 | 12.52 | 0.03311 | 0.2923 | 1.0249 | 13.20 | 0.1585 |
| 0.0800 | 0.9954 | 12.72 | 0.05248 | 0.3341 | 1.0284 | 13.23 | 0.1698 |
| 0.1002 | 1.0011 | 12.78 | 0.06026 | 0.3759 | 1.0300 | 13.29 | 0.1950 |
| 0.1044 | 1.0018 | 12.80 | 0.06310 | 0.4176 | 1.0320 | 13.32 | 0.2089 |
| 0.1211 | 1.0032 | 12.85 | 0.07080 | 0.5011 | 1.0373 | 13.40 | 0.2512 |

The data obtained on the solutions containing the arabic acid, and calculated as described above are given in Table IV.

Results:—

The errors involved in the calculation of base-combining capacity are large despite the fact that the potentiometric determinations are within the limit of experimental error. The potentiometer used is said by the manufacturers to be accurate to plus or minus 0.5 millivolts though it is not generally possible to remain in that range in the strongly alkaline solutions obtaining here.

If in the case of 0.05N sodium hydroxide one sample gave an E.M.F. of 980 millivolts and the other 980.5 millivolts the free sodium hydroxide would be 0.033 moles and 0.036 moles respectively. This would give 0.0170 moles and 0.0140 moles of base bound by a given weight of acid, i.e. an error of 20 percent. The values for moles of sodium hydroxide bound by one gram of gum given in the last column of Table IV differ by considerably more than 20 percent, but they are considered to be significant. They included a range of sodium hydroxide concentration from 0.01N to 0.24N and a range of arabic

acid concentration from 8.95 to 24.0 grams per liter. The average value from Table IV is 0.00106 moles per gram of gum from which an equivalent weight of about 1000 (943) for arabic acid is calculated. This value is in fairly good agreement with that obtained from the titration curve considering the errors involved.

TABLE IV
The alkali-combining capacity of arabic acid

| Grams of per liter | E.M.F. | pH | Con- | Orig N NaOH (N) | Free N NaOH (N') | Combd NNaOH (n) | Moles per gram of gum |
|--------------------|--------|-------|-------|-----------------|------------------|-----------------|-----------------------|
| 8.95 | 0.9207 | 11.45 | .0028 | .0131 | .0050 | .0081 | .00090 |
| | 0.9534 | 12.00 | .0100 | .0218 | .0110 | .0108 | .00121 |
| | 0.9635 | 12.19 | .0155 | .0300 | .0200 | .0100 | .00112 |
| | 0.9785 | 12.46 | .0288 | .0500 | .0400 | .0100 | .00112 |
| | 0.9913 | 12.67 | .0468 | .0800 | .0720 | .0080 | .00090 |
| | 0.9950 | 12.73 | .0537 | .1002 | .0900 | .0102 | .00114 |
| | 0.9977 | 12.76 | .0575 | .1002 | .0930 | .0072 | .00080 |
| | 1.0023 | 12.84 | .0692 | .1211 | .1150 | .0061 | .00068 |
| | 1.0091 | 12.92 | .0832 | .1503 | .1440 | .0063 | .00069 |
| | 1.0167 | 13.08 | .1202 | .2297 | .2220 | .0077 | .00086 |
| | 1.0188 | 13.10 | .1259 | .2427 | .2320 | .0107 | .00120 |
| 9.66 | 0.9623 | 12.19 | .0155 | .0300 | .0200 | .0100 | .00104 |
| | 0.8772 | 12.49 | .0309 | .0500 | .0430 | .0070 | .00073 |
| | 0.9881 | 12.68 | .0479 | .0800 | .0740 | .0060 | .00062 |
| 13.42 | 1.0082 | 12.94 | .0871 | .1670 | .1510 | .0160 | .00119 |
| | 1.0156 | 13.06 | .1148 | .2297 | .2120 | .0177 | .00132 |
| 16.00 | 0.9630 | 12.32 | .0209 | .0500 | .0270 | .0230 | .00144 |
| 19.32 | 0.9459 | 11.92 | .0083 | .0300 | .0080 | .0220 | .00114 |
| | 0.9697 | 12.32 | .0209 | .0500 | .0270 | .0230 | .00119 |
| | 0.9857 | 12.59 | .0389 | .0800 | .0580 | .0220 | .00113 |
| | 0.9904 | 12.70 | .0501 | .1102 | .0780 | .0222 | .00115 |
| | 1.0031 | 12.89 | .0776 | .1503 | .1310 | .0193 | .00100 |
| 20.00 | 0.9698 | 12.28 | .0191 | .0500 | .0240 | .0260 | .00130 |
| 24.00 | 0.9657 | 12.21 | .0162 | .0500 | .0190 | .0310 | .00129 |

The weight of evidence from the titration and alkali-combining capacity data is that a true salt, sodium arabate exists.

Osmotic Pressure as a Function of pH

Procedure:—

The method of R. S. Lillie described by Loeb¹⁴ was employed for the measurement of the osmotic pressure. Pyroxylin bags were made in a test tube of a size made by cutting in half an ordinary 6" by 1" test tube. The bags were prepared uniformly, that is by filling with collodion (Merck, 275 grains of ether per ounce, 27 percent alcohol, U.S.P. IX). The collodion was then poured slowly from the flask by rotating the latter. The process was timed to take 30 seconds. The flask with its adhering layer of collodion was then allowed to dry for fifteen minutes at room temperature, after which

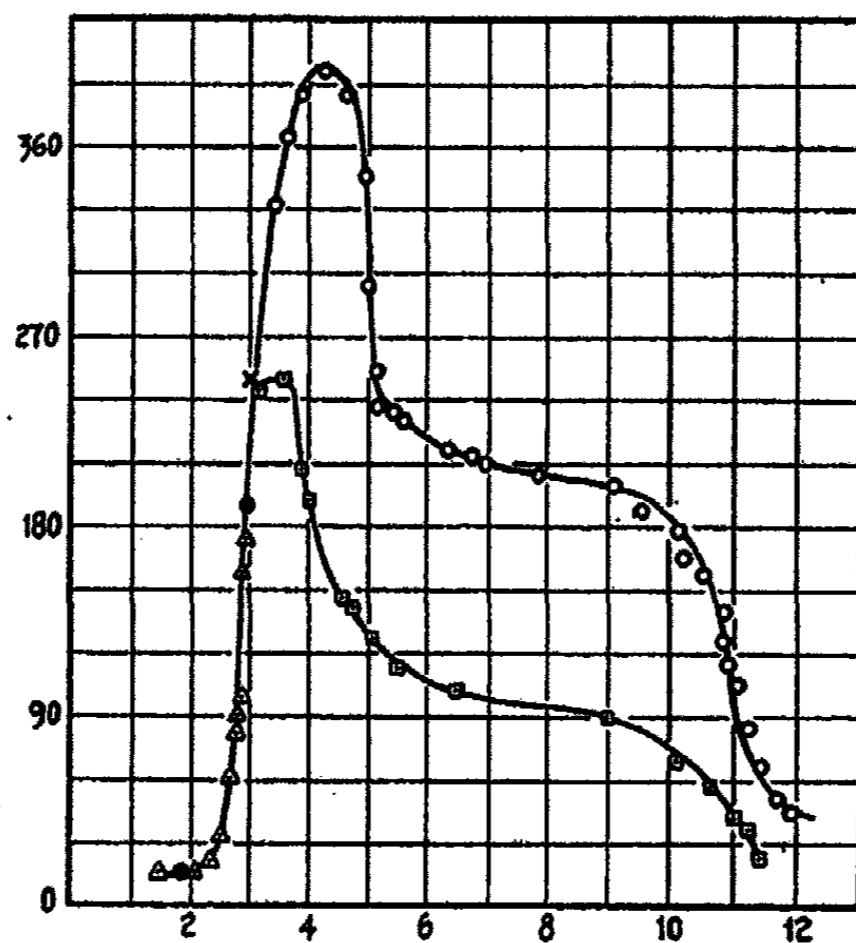


FIG. 2

Osmotic pressure as a function of pH.

$\Delta - \Delta = \text{HCl}$. $\bullet - \bullet = \text{H}_2\text{PO}_4$. $\times = \text{H}_2\text{O}$. $\circ - \circ = \text{NaOH}$. $\square - \square = \text{Ba(OH)}_2$.
 Abscissae = pH.
 Ordinates = Osmotic pressure in millimeters of solution.

water was allowed to run in slowly for five minutes. The bags were closed by tying with string to a one-hole rubber stopper. The bag was filled with the solution with the aid of a small funnel, all air bubbles were removed and a glass tube was pushed into the bag, through the stopper to serve as a manometer. The manometer and bag were inserted in a 400 cc wide-mouthed bottle containing 350 cc of solution by means of a two-holed rubber stopper. The solutions in the bottle and inside the manometer tubes were protected from the carbon dioxide of the air by means of soda-lime tubes. The surface of the stopper was so adjusted that it lay in the surface of the solution in the bottle. This apparatus was kept at 25°C by immersion in a water thermostat during the course of a measurement.

The water diffused from the outside bottle into the arabic acid solution, and the column of liquid in the manometer rose to a maximum usually reached in about 10 hours. Due to the fact that the pyroxylin bag is impermeable to the gum, a change in pH will occur due to the Donnan membrane equilibrium. It is true also that the solution inside the bag is diluted by the entrance of water into the collodion bag. Such a condition is met by filling the manometer tube to a point indicated as the osmotic equilibrium by preliminary experiments. It was not thought that such a procedure would be advantageous however, since it would undoubtedly retard uniform diffusion of the inside solution, and introduce as great an error as that caused by dilu-

TABLE V
Osmotic pressure as a function of pH

| | Outside solution | | Inside solution | | Obs. osmotic press. in mm. of solution |
|------|------------------|-------|-----------------|-------|----------------------------------------------|
| | E.M.F. | pH | E.M.F. | pH | |
| NaOH | | | | | |
| 1. | 0.5823 | 5.72 | 0.4457 | 3.37 | 331 |
| 2. | 0.5865 | 5.79 | 0.4608 | 3.63 | 363 |
| 3. | 0.5892 | 5.83 | 0.4682 | 3.77 | 384 |
| 4. | 0.7763 | 9.09 | 0.4958 | 4.24 | 396 |
| 5. | 0.8343 | 10.06 | 0.5156 | 4.58 | 384 |
| 6. | 0.8413 | 10.16 | 0.5350 | 4.92 | 342 |
| 7. | 0.8486 | 10.26 | 0.5383 | 4.96 | 292 |
| 8. | 0.8768 | 10.72 | 0.5448 | 5.06 | 252 |
| 9. | 0.8705 | 10.77 | 0.5508 | 5.17 | 235 |
| 10. | 0.8821 | 10.81 | 0.5629 | 5.37 | 234 |
| 11. | 0.8848 | 10.83 | 0.5688 | 5.50 | 229 |
| 12. | 0.8878 | 10.84 | 0.6113 | 6.18 | 215 |
| 13. | 0.8857 | 10.88 | 0.6396 | 6.70 | 213 |
| 14. | 0.8853 | 10.83 | 0.6502 | 6.86 | 208 |
| 15. | 0.8813 | 10.74 | 0.7116 | 7.91 | 204 |
| 16. | 0.8934 | 10.97 | 0.7800 | 9.07 | 198 |
| 17. | 0.8953 | 11.00 | 0.8022 | 9.46 | 187 |
| 18. | 0.8973 | 11.11 | 0.8399 | 10.15 | 177 |
| 19. | 0.8960 | 11.09 | 0.8436 | 10.18 | 164 |
| 20. | 0.9013 | 11.16 | 0.8429 | 10.19 | 163 |
| 21. | 0.9004 | 11.15 | 0.8615 | 10.46 | 156 |
| 22. | 0.9085 | 11.29 | 0.8800 | 10.85 | 137 |
| 23. | 0.9142 | 11.37 | 0.8867 | 10.90 | 112 |
| 24. | 0.9157 | 11.41 | 0.8927 | 11.03 | 103 |
| 25. | 0.9083 | 11.27 | 0.8793 | 10.79 | 125 |
| 26. | 0.9220 | 11.60 | 0.9000 | 11.22 | 83 |
| 27. | 0.9332 | 11.46 | 0.9186 | 11.44 | 64 |
| 28. | 0.9398 | 11.90 | 0.9313 | 11.74 | 50 |
| 29. | 0.9524 | 12.01 | 0.9447 | 11.89 | 44 |

TABLE V (cont'd)
 Osmotic pressure as a function of pH

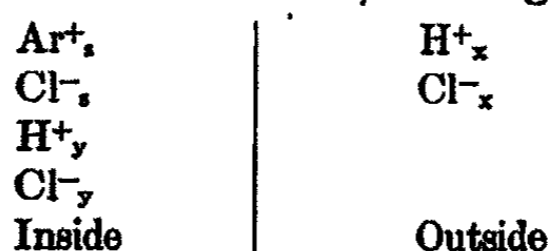
| | Outside solution E.M.F. | pH | Inside solution E.M.F. | pH | Obs. osmotic press in mm. of solution |
|------------|----------------------------|-------|---------------------------|-------|---------------------------------------------|
| H_2O | | | | | |
| 30. | 0.5567 | 5.28 | 0.4262 | 3.05 | 248 |
| $Ba(OH)_2$ | | | | | |
| 31. | 0.5517 | 5.19 | 0.4322 | 3.15 | 244 |
| 32. | 0.6072 | 6.14 | 0.4442 | 3.35 | 247 |
| 33. | 0.5716 | 5.53 | 0.4828 | 4.01 | 191 |
| 34. | 0.7137 | 7.98 | 0.4752 | 3.88 | 205 |
| 35. | 0.7628 | 8.84 | 0.5177 | 4.61 | 145 |
| 36. | 0.7858 | 9.19 | 0.5238 | 4.71 | 142 |
| 37. | 0.7638 | 8.85 | 0.5476 | 5.10 | 126 |
| 38. | 0.8160 | 9.73 | 0.5708 | 5.53 | 110 |
| 39. | — | — | 0.6259 | 6.46 | 102 |
| 40. | 0.8537 | 10.38 | 0.7791 | 9.07 | 88 |
| 41. | 0.8822 | 10.84 | 0.8426 | 10.16 | 67 |
| 42. | 0.8916 | 11.00 | 0.8697 | 10.62 | 55 |
| 43. | 0.9058 | 11.23 | 0.8924 | 11.03 | 41 |
| 44. | 0.9141 | 11.38 | 0.9028 | 11.20 | 36 |
| 45. | 0.9275 | 11.58 | 0.9198 | 11.40 | 23 |
| HCl | | | | | |
| 46. | 0.3322 | 1.45 | 0.3322 | 1.45 | 14 |
| 47. | 0.3396 | 1.56 | 0.3408 | 1.56 | 14 |
| 48. | 0.3497 | 1.74 | 0.3508 | 1.75 | 14 |
| 49. | 0.3668 | 2.03 | 0.3658 | 2.01 | 15 |
| 50. | 0.3726 | 2.21 | 0.3738 | 2.14 | 16 |
| 51. | 0.3885 | 2.45 | 0.3840 | 2.32 | 21 |
| 52. | 0.4064 | 2.70 | 0.3928 | 2.47 | 32 |
| 53. | 0.4249 | 3.02 | 0.4026 | 2.64 | 60 |
| 54. | 0.4400 | 3.28 | 0.4115 | 2.79 | 82 |
| 55. | 0.4450 | 3.37 | 0.4143 | 2.84 | 98 |
| 56. | 0.4372 | 3.24 | 0.4117 | 2.80 | 87 |
| 57. | 0.4836 | 4.03 | 0.4223 | 2.98 | 174 |
| 58. | 0.4764 | 3.91 | 0.4202 | 2.94 | 159 |
| H_3PO_4 | | | | | |
| 59. | 0.3544 | 1.82 | 0.3538 | 1.81 | 14 |
| 60. | 0.3610 | 1.93 | 0.3607 | 1.93 | 15 |
| 61. | 0.3790 | 2.24 | 0.3763 | 2.19 | 16 |
| 62. | 0.4013 | 2.62 | 0.3903 | 2.43 | 30 |
| 63. | 0.4392 | 3.26 | 0.4083 | 2.74 | 97 |
| 64. | 0.4764 | 3.89 | 0.4185 | 2.91 | 189 |

tion. The heights* in the manometer tubes were recorded and the pH values of the solutions determined at the end of twenty-four hours.

Table V gives the data for the osmotic pressure and pH of solutions of originally one percent solutions of arabic acid, with two different bases, sodium hydroxide and barium hydroxide. This is shown graphically in Fig. 2.

The osmotic pressure is a maximum at a pH of 4.25, in the case of sodium arabate and 3.35 for barium arabate. The points for the two acids used lie on the same curve. The osmotic pressure of 248 mm. at pH = 3.05, is that of the pure gum solution in distilled water, to which neither acid nor base had been added. There is no evidence of an isoelectric point as is found in the case of proteins. At a pH of about 1.90 the curve is parallel to the abscissa; that is, the osmotic pressure has become constant and is due to molecules or particles of gum. Between the pH values of 5.0 and 10.0, the neutrality region, a flat portion of the curve is observed.

If the gum did not combine with the acid, according to the picture



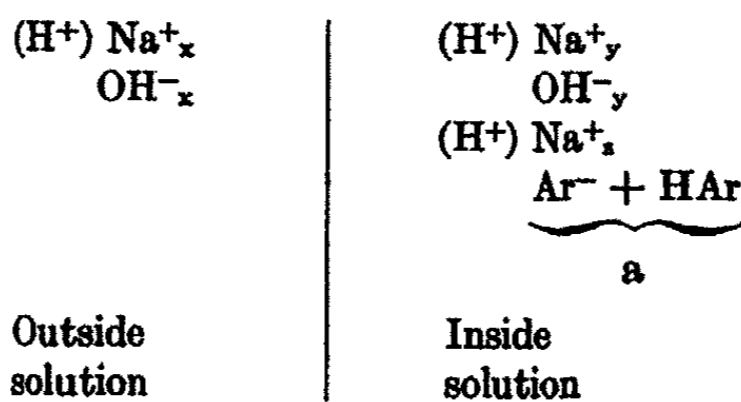
we should find the concentration of hydrogen ion greater in the outside than in the inside solution because from the equation $x^2 = y(y + z)$, x must be greater than y . Such a condition was never found. Below a pH of 1.90 the hydrogen ion concentrations of the inside and outside solutions are identical, indicating that the gum did not combine with the acid.

The nature of the curves suggested that the membrane theory of Donnan might be applied, since both show a maximum osmotic pressure at a definite pH and fall away on both sides of the maximum point while the curve for the barium arabate falls below that of the sodium arabate.

One may examine qualitatively the effects of adding acid or alkali to the system by means of the osmotic pressure equation,—

$$\text{o.p.} = (2y + z - 2x)RT \tag{I}$$

Picture the system as follows:—



* The difference in elasticity of the pyroxylin bags, subjected to varying pressures at the several heights also introduces an error, but the smoothness of the curve plotted, where the heights in millimeters are used, indicates that the error is not great.

From the Donnan theory then $x^2 = y(y + z)$ or $x = \sqrt{y(y + z)}$. Substituting this value of x in equation (I) above

$$\text{o.p.} = (2y + z - 2\sqrt{y(y + z)})RT$$

At a pH of 2.0, Fig. 3 and Table VI, x and y are equal, hence z must be zero since $z = \frac{(x + y)(x - y)}{y}$, and the observed osmotic pressure of 14

millimeters of solution is due to a . As y increases, z increases due to the formation of ionized arabic acid, or sodium arabate. At first z increases more rapidly than y , or until z has reached its limiting value fixed by the original concentration of arabic acid. From equation (I) the osmotic pressure must be a maximum at this point, and with increasing y , z becomes negligible in comparison to y , and the osmotic pressure diminishes approaching zero as its limit. It would be valuable to determine whether or not a point might be reached where x and y would again be equal, but the determination was not realized experimentally. The collodion bags dissolved in solutions more strongly alkaline than those used. The validity of the Donnan theory is apparently borne out further by the fact that at the same pH (4.25) the point on the barium arabate curve is about one half as high as that on the sodium arabate curve, which is what the theory demands, viz. for a monovalent cation equation (I) expresses the osmotic pressure, while for a divalent cation the

$$\text{o.p.} = 3/2y + z/2 - 3/2x.$$

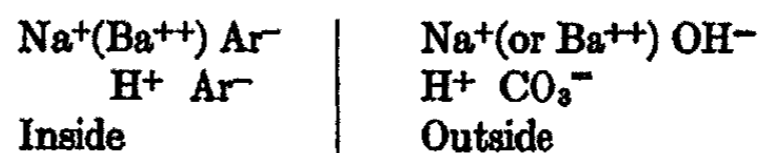
There is no reason for thinking that the barium arabate is but half as highly ionized as sodium arabate.

A few experiments were conducted to show the effect of varying concentrations of a neutral salt, (sodium chloride) on the osmotic pressure of the arabic acid solutions. The results indicated that the osmotic pressure was depressed by the presence of neutral salt as was expected from a consideration of the Donnan theory.

Using the data in Table V, an attempt was made to calculate the osmotic pressure based on the following considerations. The inside solution was separated from the outside solution by a membrane impermeable to one of the ions, namely arabate ion, existing in the solution, thus giving rise, at equilibrium to an unequal distribution of ions across the membrane. The observed osmotic pressure was then the difference between the osmotic pressure of the inside solution, and the counter osmotic pressure of the outside solution.

The equilibria obtaining in the several cases are represented as follows.

Where both the inside and outside solutions are acid in the presence of sodium hydroxide (or barium dioxide) the picture is



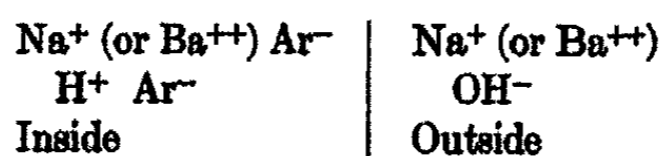
Where both the inside and outside solutions are acid in the presence of hydrochloric acid, the picture is



In the special case of a one per cent solution of arabic acid, where both the inside and outside solutions are acid, the picture is



Where the inside solution is acid and the outside solution is alkaline, the picture is



Where both the inside and outside solutions are alkaline, the picture is



A typical calculation using data in the first horizontal row of Table V is as follows. In this case both the inside and outside solutions are acid in the presence of sodium hydroxide.

| Inside | Outside |
|-----------------------------------------------------------------------------------------|-----------------------------------------------------------|
| $C_{Na^+} = 52 \times 10^{-5}$ m.p.l. from Fig. 1 | $C_{Na^+} = C_{OH^-} = 5.25 \times 10^{-5}$ |
| $C_{H^+} = 42.7 \times 10^{-5}$ m.p.l. | $C_{H^+} = 0.19 \times 10^{-5}$ |
| $C_{HAr} = 89.0 \times 10^{-5} - 42.7 \times 10^{-5} =$ 46.3×10^{-5} m.p.l. | $C_{CO_3^{2-}} = 0.10 \times 10^{-5}$ |
| Total ion conc. inside = 141×10^{-5} m.p.l. | Total ion conc. outside = 0.29×10^{-5} m.p.l. |

Hence the osmotic pressure of the system is due to a concentration of ions equal to $141 \times 10^{-5} - 0.29 \times 10^{-5} = 140.71 \times 10^{-5}$ m.p.l. If the theoretical osmotic pressure of a gram molecular solution is expressed in terms of a column of water we get, at 25° C,

$$22.4 \times 760 \times 13.6 \times 298/273 = 2.5 \times 10^5 \text{ m.m.}$$

or in other words a theoretical pressure of 2.5 m.m. corresponds to a concentration of 10^{-5} normal. The calculated osmotic pressure is then

$$[140.71 \times 10^{-5}] [2.5 \times 10^5] = 352 \text{ m.m.}$$

whereas the observed value was 331 m.m.

Typical results of the calculations based on the data in Table V and the foregoing pictures of the equilibria are given in Table VI.

* The concentration of $HAr = H^+ + Ar^- = 89.0 \times 10^{-5}$ m.p.l. calculated from potentiometric measurement of 1% solution. Table VI.

TABLE VI

| Inside Sol- ution | | Outside sol- ution | | C inside C outside $\times 10^{-4}$ | Calc. Osm. Press. (V) \times 2.5 \times $\times 10^{-3}$ (VI) | Obs. Osm. Press. (VII) |
|----------------------|-----------------------------------------------------|-----------------------|-----------------------------------------------------|-------------------------------------------|-------------------------------------------------------------------------------------|---------------------------------|
| pH (I) | Conc. ions m.p.l. $\times 10^{-3}$ (II) | pH (III) | Conc. ions m.p.l. $\times 10^{-3}$ (IV) | | | |
| H ₂ O | | | | | | |
| 3.05 | 89.0 | 5.28 | 0.78 | 88.22 | 221 | 248 |
| NaOH | | | | | | |
| 3.37 | 141.00 | 5.72 | 0.29 | 140.71 | 352 | 331 |
| 3.63 | 149.00 | 5.79 | 0.24 | 148.76 | 372 | 363 |
| 3.77 | 155.00 | 5.83 | 0.22 | 154.78 | 387 | 384 |
| 4.24 | 163.00 | 9.09 | 2.46 | 160.54 | 401 | 396 |
| 4.58 | 166.00 | 10.06 | 23.00 | 143.00 | 358 | 384 |
| 4.92 | 168.00 | 10.16 | 28.80 | 139.20 | 348 | 342 |
| 4.96 | 169.00 | 10.26 | 36.40 | 132.60 | 332 | 292 |
| 5.06 | 170.00 | 10.72 | 105.00 | 65.00 | 163 | 252 |
| 5.17 | 170.00 | 10.77 | 117.60 | 52.40 | 131 | 235 |
| 5.37 | 171.00 | 10.81 | 129.20 | 41.80 | 105 | 234 |
| 5.50 | 171.00 | 10.83 | 135.20 | 35.80 | 90 | 229 |
| 6.18 | 172.00 | 10.84 | 138.40 | 33.60 | 84 | 215 |
| 6.70 | 172.00 | 10.88 | 151.08 | 20.92 | 52 | 213 |
| 6.86 | 172.00 | 10.83 | 135.20 | 36.81 | 92 | 208 |
| 9.07 | 175.40 | 10.97 | 186.80 | -11.40 | -29 | 198 |
| 9.46 | 178.76 | 11.00 | 200.00 | -21.24 | -53 | 187 |
| 10.15 | 203.00 | 11.11 | 258.00 | -55.00 | -138 | 177 |
| 11.89 | 1791.00 | 12.01 | 2060.00 | -269.00 | -673 | 44 |
| Ba(OH) ₂ | | | | | | |
| 3.15 | 109.50 | 5.19 | 0.97 | 108.53 | 272 | 244 |
| 3.35 | 113.50 | 6.14 | 0.11 | 113.39 | 284 | 247 |
| 4.01 | 124.00 | 5.53 | 0.44 | 123.56 | 309 | 191 |
| 3.88 | 123.00 | 7.98 | 0.14 | 122.86 | 307 | 205 |
| 4.61 | 128.00 | 8.84 | 1.05 | 126.95 | 317 | 145 |
| 4.71 | 128.50 | 9.19 | 2.23 | 126.27 | 316 | 142 |
| 5.10 | 129.50 | 8.85 | 1.16 | 128.34 | 321 | 126 |
| HCl | | | | | | |
| 2.94 | 141.00 | 3.91 | 24.60 | 116.40 | 291 | 159 |
| 2.80 | 229.00 | 3.24 | 115.00 | 114.00 | 285 | 87 |
| 2.79 | 235.00 | 3.28 | 105.00 | 130.00 | 325 | 82 |
| 2.47 | 589.00 | 2.70 | 400.00 | 189.00 | 473 | 32 |
| 2.01 | 1865.00 | 2.03 | 1868.00 | -3.00 | -7.5 | 15 |
| 1.45 | 7011.00 | 1.45 | 7100.00 | -89.00 | -222.5 | 14 |

As seen in Table VI, in the case of the 1% solution of arabic acid in distilled water, the calculated value for the osmotic pressure agrees closely with the observed value. This agreement is good likewise in the systems (1) where in the presence of sodium hydroxide (or barium hydroxide) both inside and outside solutions are acid, and (2) where in the presence of sodium hydroxide (or barium hydroxide), the inside solution is acid and the outside solution is slightly alkaline.

With increasing alkalinity in the outside solution, the divergence increases; and when both the inside and outside solutions become alkaline, the differences between the calculated and observed values are very large.

These marked differences may be due to a partial hydrolysis of the arabate ion in the strong alkaline solutions, or to a reaction between the alkali and the pyroxylin membranes, or both. It has been stated previously that the membranes disintegrated in the strongly alkaline solutions, and even in those cases, where results were reported, the bags became tender in twenty-four hours.

Where both the inside and outside solutions were acid in the presence of hydrochloric acid, the calculated values do not agree with the observed values. This lack of agreement is due probably to the fact that neither solution was analyzed for chloride and hence there is no measure of the equilibrium $\text{HAr} \rightleftharpoons \text{H}^+ + \text{Ar}^-$ which in distilled water indicates a concentration of 89.0×10^{-5} m.p.l. or a calculated osmotic pressure of 221 m.m. and in strong hydrochloric acid, where the pH values of both inside and outside solutions are identical, a calculated concentration of 5.6×10^{-5} m.p.l. from the observed osmotic pressure of 14 m.m.

The close agreement of the calculated and observed values in the cases not complicated by strong alkali indicates the validity of the pictures presented to show the equilibria. That is, there is an unequal distribution of ions across the semipermeable membrane and the arabate ion combines quantitatively with both sodium and barium ions.

Viscosity as a Function of pH

Introductory:—

In his work on the proteins, Loeb pointed out the very similar nature of the curves obtained when several of their properties such as osmotic pressure, membrane potentials, swelling and viscosity were considered as a function of pH. That is, in almost every case, starting with the isoelectric protein he was able to show a rise to a maximum on both sides of the isoelectric point when the property was plotted as a function of pH, and a subsequent decrease in the value of the property with increasing acidity or alkalinity. The curves obtained in the osmotic pressure study of alkaline arabate solutions, (Fig. 2) are similar in nature to those obtained by Loeb with proteins, in so far as the colloidal molecule functions as an anion. Viscosity of arabate solutions as a function of pH is not unlike the osmotic pressure pH curve. In neither case was evidence for an arabic cation found.

The viscosity of a solution has been definitely shown to be a function of the volume of the solute in the solution,¹⁴ or what is the same thing, a function of the free volume of the solute.¹¹ The free volume is the difference between the volume occupied by the molecules, and that volume filled by the molecules on the assumption of tetrahedral close packing.

The increase and decrease in viscosity of the gum arabic acid solution must depend then upon some mechanism whereby the molecules may increase and decrease their volume.

When gum arabic is dissolved in water, it swells to some extent before going into solution. Further it is well known that gum arabic may be ren-

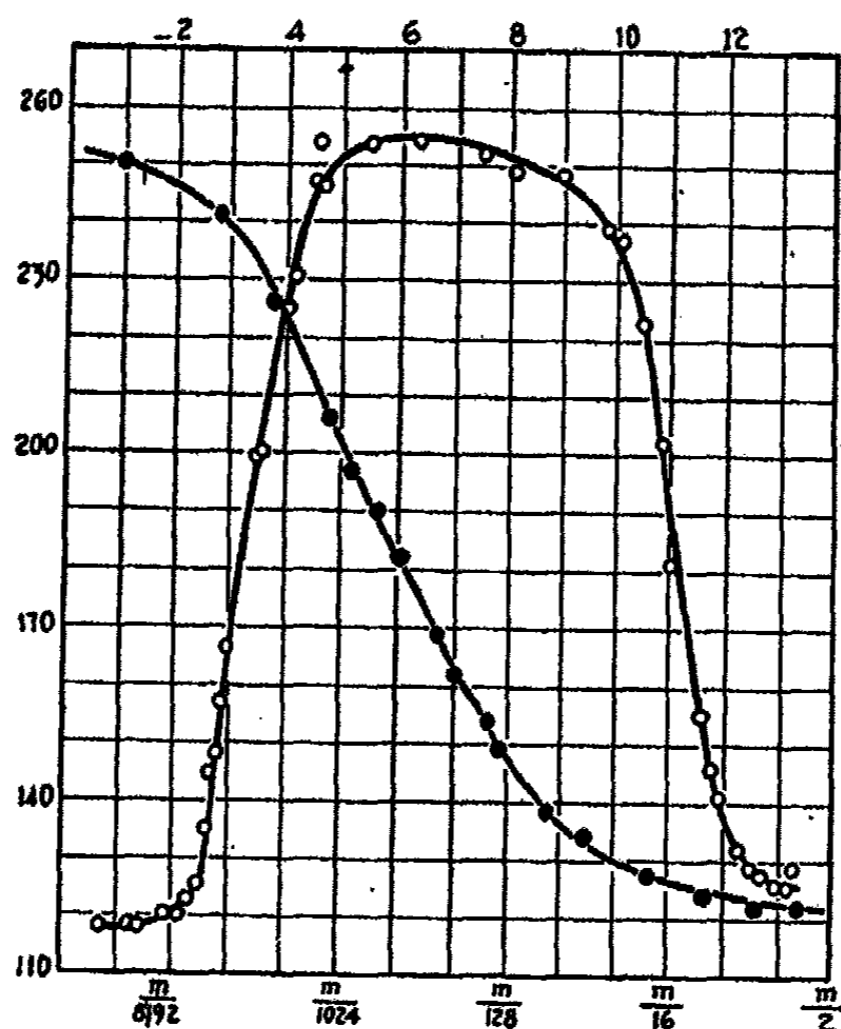


FIG. 3

Viscosity as a function of pH and of neutral salt concentration. ● - ● = Effect of sodium chloride. ○ - ○ = effect of pH.
 Top abscissae = pH. Bottom abscissae = Concentration of salt.
 Ordinates = Viscosity ratio (water = 100).

dered insoluble by extreme drying either with alcohol or by heating. When it is thus dried, the gum swells in water to a jelly-like mass which does not dissolve except on long standing. We have here evidence of swelling, hence a mechanism by which the gum arabic acid may increase or decrease its relative volume in the solution.

According to Procter and Wilson the force which causes swelling is an osmotic force, i.e. the diffusion of water through a membrane. In this case the membrane is the arabate ions or aggregates, and the forces which limit the swelling are the cohesive forces obtaining between the arabate ions.

Procedure:—

The time of the outflow of the gum arabic acid solution through an Ostwald viscometer, was measured at 25°C. The quotient of this time divided by the time of outflow of water through the same tube and at the same temperature is referred to as the viscosity ratio of the gum arabic acid solution. The viscosity ratio was determined for one percent gum arabic acid solutions over a range of pH from 0.74 to 13.33 obtained by using hydrochloric acid, and sodium hydroxide. A series was not run using a divalent cation, Ba⁺⁺, because of the experimental difficulties involved in the handling of the barium arabate solutions, containing an excess of barium hydroxide.

In Table VII are given data obtained by measuring the time of outflow immediately after the solutions were prepared. In Table VIII are given data obtained by measuring the time of outflow 15 hours after the solutions were prepared. Inasmuch as the purified stock of gum arabic acid must be kept in solution, the possibility of learning whether swelling, hence viscosity increases on standing was precluded. Since the data for both series lie on the same curve, Fig. 3, the results do confirm the resistance of the gum arabic

TABLE VII
Viscosity as a function of pH

| Acid or alkali | E.M.F. | pH | Viscosity ratio | Acid or alkali | E.M.F. | pH | Viscosity ratio |
|----------------|------------------|--------|-----------------|----------------|--------|--------|-----------------|
| HCl | 0.2892 | 0.74 | 1.18 | NaOH | 0.5722 | 5.50 | 2.54 |
| | 0.3167 | 1.22 | 1.18 | | 0.6191 | 6.30 | 2.54 |
| | 0.3216 | 1.28 | 1.18 | | 0.6916 | 7.51 | 2.52 |
| | 0.3256 | 1.35 | 1.19 | | 0.7248 | 8.14 | 2.49 |
| | 0.3293 | 1.41 | 1.18 | | 0.7757 | 9.00 | 2.48 |
| | 0.3615 | 1.94 | 1.20 | | 0.8296 | 9.85 | 2.39 |
| | 0.3748 | 2.17 | 1.21 | | 0.8456 | 10.17 | 2.37 |
| | 0.3821 | 2.29 | 1.23 | | 0.8694 | 10.56 | 2.23 |
| | 0.3910 | 2.44 | 1.26 | | 0.8926 | 10.96 | 2.02 |
| | 0.4013 | 2.62 | 1.35 | | 0.9032 | 11.14 | 1.81 |
| | 0.4062 | 2.70 | 1.45 | | 0.9307 | 11.59 | 1.55 |
| | | | | | 0.9424 | 11.79 | 1.46 |
| | H ₂ O | 0.4062 | 2.70 | | 1.44 | 0.9513 | 11.94 |
| NaOH | 0.4123 | 2.81 | 1.48 | 0.9726 | 12.31 | 1.32 | |
| | 0.4166 | 2.88 | 1.57 | 0.9849 | 12.52 | 1.29 | |
| | 0.4244 | 3.01 | 1.66 | 0.9927 | 12.66 | 1.28 | |
| | 0.4524 | 3.49 | 1.97 | 1.0167 | 12.98 | 1.26 | |
| | 0.4583 | 3.59 | 2.01 | 1.0247 | 13.07 | 1.26 | |
| | 0.4826 | 3.99 | 2.25 | 1.0332 | 13.19 | 1.26 | |
| | 0.4921 | 4.16 | 2.31 | 1.0421 | 13.33 | 1.29 | |
| | 0.5136 | 4.53 | 2.47 | | | | |
| | 0.5172 | 4.58 | 2.54 | | | | |
| | 0.5200 | 4.65 | 2.46 | | | | |

acid to hydrolysis. In connection with this work the specific rotatory power was measured at the different pH values, and was found not to be dependent upon them. The specific rotatory power is indeed identical with that of the purified gum arabic acid stock solution in every case.

TABLE VIII
Viscosity as a function of pH (15 hours)

| Acid or alkali | E.M.F. | pH | Viscosity ratio | Acid or alkali | E.M.F. | pH | Viscosity ratio |
|------------------|--------|-------|-----------------|----------------|--------|-------|-----------------|
| HCl | 0.3026 | 0.96 | 1.19 | NaOH | 0.8595 | 10.38 | 2.14 |
| | 0.3290 | 1.41 | 1.18 | | 0.9008 | 11.09 | 1.91 |
| | 0.3816 | 2.28 | 1.21 | | 0.9206 | 11.38 | 1.64 |
| H ₂ O | 0.4072 | 2.71 | 1.49 | | 0.9616 | 12.12 | 1.33 |
| | | | | | 1.0018 | 12.79 | 1.25 |
| | | | | | 1.0316 | 13.30 | 1.22 |
| NaOH | 0.5186 | 4.60 | 2.50 | | 1.0484 | 13.51 | 1.29 |
| | 0.5219 | 4.66 | 2.51 | | | | |
| | 0.6950 | 7.60 | 2.54 | | | | |
| | 0.8534 | 10.26 | 2.47 | | | | |

Results:—

The data lie on a smooth curve the maximum point of which is a viscosity ratio of 2.54 at pH = 4.58 to 6.30. In the region between pH = 5 and 10 this curve, as well as those of the titration and osmotic pressure—pH curves, indicates a gradual change in property with marked change in pH.

Since the Donnan theory was applied qualitatively in the case of osmotic pressure it was attempted to make the same application here. The theory demands the presence of a membrane impermeable to at least one ion, a condition satisfied in the osmotic pressure work by the collodion membrane impermeable to the arabate ion. In the case of viscosity the arabate particles themselves act as the membrane. They are held together as suggested by cohesive forces. They cannot diffuse then, and hence effect no appreciable osmotic pressure. The Na⁺ or H⁺ ions held to them by electrostatic attraction can diffuse and hence exercise osmotic pressure. Conditions are right then for the establishment of the Donnan membrane equilibrium. Let e represent the osmotic force which causes swelling. Then

$$e = 2y + z^2 - x$$

an equation identical with that for osmotic pressure discussed in the previous section.

Now from the Donnan equation

$$y = \frac{-z + \sqrt{z^2 + 4x^2}}{2}$$

Substituting this value of y in the above equation we have

$$e = -2x + \sqrt{(4x^2 + z^2)} \quad (II)$$

We may picture the system exactly as was done under the discussion osmotic pressure.

Starting at a pH of 2.0, Fig. 2, as before, as x increases, that is decreasing concentration of hydrogen ion, z also increases and at a faster rate than x , until its limiting value is reached. The value of z is limited by the concentration of gum arabic acid in the solution. If the ionization of gum arabic acid or of sodium arabate were sufficiently repressed by increasing x (addition of sodium hydroxide) then z would diminish. In any case, taking the last term of equation (II) above

$$\lim_{x = \infty} \sqrt{4x^2 + z^2} = \sqrt{4x^2}$$

from which

$$\lim_{x = \infty} e = 0$$

showing that as x increases, e increases to a maximum and then decreases. The conclusion would be true whether or not the ionization of the sodium arabate was extensively repressed.

The data and curve show very definitely the increase of the viscosity ratio from a minimum to a maximum with a subsequent decrease. This behavior, the change of viscosity with hydrogen ion concentration, is thus qualitatively in accordance with the Donnan membrane equilibrium.

The Effect of Neutral Salts on Viscosity

The properties, osmotic pressure and viscosity, of arabic acid solutions have been shown to be a function of the hydrogen ion concentrations of the solutions, and further the behavior has qualitatively followed the Donnan theory. So far the behavior of the carbohydrate, arabic acid, has been shown to be very like that of proteins in respect to the conditions and explanations mentioned.

Several observers, Hofmeister, Pauli, Sackur, Lillie, and Loeb, have remarked that neutral salts depressed these properties of proteins, and it was shown by Loeb that when the measurements were made at the same hydrogen ion concentration, the results were explained by the Donnan theory.

Procedure:—

To 0.25 gram of gum arabic acid in a 25 cc volumetric flask, sufficient 0.1N sodium hydroxide was added to bring it to a pH of 7.85. Varying amounts of a sodium chloride solution previously brought to a pH of 7.85 by sodium hydroxide were then added to the flasks. The solutions in the flasks were brought to volume by the addition of water having a pH of 7.85, obtained by using sodium hydroxide. In such a manner one percent solutions of arabic acid, containing varying concentrations of sodium chloride and having the same pH value were obtained.

The viscosity ratios of the solutions were then measured in the manner hitherto described. The data are given in Table IX, and are plotted in Fig. 3.

Results:—

The curve shows that the viscosity is depressed by neutral salts, the more, the greater the concentration of the salt. This behavior may be explained on the basis of the Donnan theory using the picture just given. That is, in the case at hand, when sodium chloride is added to a sodium arabate solution both x and y are increased, that is, the Na^+ in the outside solution and the Na^+ ions which are not in combination with the arabate ions, in the inside solution. The concentration, z , of Na^+ in combination with the arabate ions remains the same at the same pH (neglecting repression of ionization of sodium arabate). Further x , is greater than y always. As x increases, approaching infinity as a limit, the viscosity decreases continuously to zero.

Again the experimental facts confirm what might have been predicted from a qualitative consideration of the Donnan theory. The marked change in viscosity with change in pH value, as well as the depression of the viscosity by sodium chloride, indicates that gum arabic exists in the form of micells like gelatin.

TABLE IX

Viscosity as a function of neutral salt concentration* at the same hydrogen ion concentration

| Molarity | Viscosity ratio | Molarity | Viscosity ratio |
|----------------|-----------------|---------------|-----------------|
| 0 | 2.50 | 1/166 (.0060) | 1.54 |
| 1/5000 (.0002) | 2.41 | 1/143 (.0070) | 1.49 |
| 1/2500 (.0040) | 2.26 | 1/71 (.0140) | 1.38 |
| 1/1250 (.0008) | 2.06 | 1/50 (.0200) | 1.34 |
| 1/825 (.0012) | 1.97 | 1/20 (.0500) | 1.27 |
| 1/625 (.0016) | 1.90 | 1/10 (.1000) | 1.24 |
| 1/500 (.0020) | 1.82 | 1/5 (.2000) | 1.22 |
| 1/333 (.0030) | 1.69 | 1/3 (.3333) | 1.22 |
| 1/250 (.0040) | 1.62 | | |

*pH = 7.85.

Summary

A study of certain phases of the physico-chemical behavior of the colloidal polysaccharide, gum arabic, is offered. In the report a method of purification has been described and certain properties investigated.

The equivalent weight of the acid was found to be about 1200 from its base-combining capacity measured by titration with sodium and barium hydroxides, and about 1000 when varying concentrations of alkali and arabic acid were used in measuring the base-combining capacity.

The nature of the titration curve and the agreement of the equivalent weight of arabic acid calculated from it, with that value obtained from a measurement of the base-combining capacity, indicate that the reaction between arabic acid and alkalis is a simple chemical combination involving primary valence forces.

The calculated values of the osmotic pressure based on potentiometric measurements are in fair agreement with the observed values within the limits of accuracy of the technique and provided the solutions are not too alkaline. The qualitative application of the Donnan theory to the results obtained when osmotic pressure and viscosity were measured as a function of hydrogen ion and neutral salt concentrations was successful, and accounted for the nature of the curves, in short its colloidal behavior.

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THE PREPARATION OF A LEAD SELENIDE HYDROSOL

BY J. BROOKS

The present paper describes the preparation of a colloidal solution of lead selenide. As some of the factors involved are not without interest for colloid formation in general the method is described in detail.

It was desired that the sol should possess the following properties:—

(a) that it should contain a fairly high concentration of colloid (up to 0.5 per cent lead as lead selenide.)

(b) that it should be free from any but negligible amounts of ionic lead.

(c) that it should be stable on boiling in the presence of 1.0 per cent sodium chloride.

The usual methods for the preparation of colloidal metallic sulphides were first used, employing hydrogen selenide in place of hydrogen sulphide; these were:

(A) the action of H_2Se on aqueous solutions of lead salts.

(B) the action of H_2Se on freshly precipitated lead hydroxide or lead selenide suspended in water.

As the dilute sols thus obtained were flocculated by $NaCl$, gelatin was used as a protective agent and the same experiments were repeated in the presence of 0.5 per cent of this substance.

The action of H_2Se on $PbSe$ suspended in the gelatin solution gave a sol containing only 0.06 per cent Pb (as $PbSe$). With suspended lead hydroxide more concentrated sols were obtained, but the conversion of hydroxide into selenide was slow. Ultra-filtration showed that both sols contained negligible amounts of ionic lead. The passage of H_2Se into a solution of lead acetate and gelatin gave stable sols but ultra-filtration showed that they contained ionic lead in concentrations which increased with the initial concentration of lead acetate used. This was apparently due to the presence of the acetic acid formed.¹



Sufficient sodium bicarbonate to neutralise the acetic acid produced was therefore added before the removal of excess H_2Se .

Experimental

The method used was as follows. Air was first removed² from a boiling solution of lead acetate containing 0.5 per cent gelatin by the passage of nitrogen through the apparatus. After cooling the solution to room tempera-

¹ Before ultra-filtration the excess H_2Se present at the end of the reaction was removed by bubbling with nitrogen. In the presence of acetic acid continued removal of H_2Se would lead to a reversal of the above reaction with a consequent increase of the amount of Pb^{++} present.

² This is rendered necessary by the rapid oxidation of hydrogen selenide to selenium by atmospheric oxygen.

ture H_2Se (generated by the action of H_2O on phosphorus selenide at 100°) was led into the stirred solution (300-400 revolutions per minute). After the passage of excess H_2Se the calculated amount of $N/2 NaHCO_3$ was added to neutralise the acetic acid present. The excess of toxic gas was then removed by raising the sol to boiling point during the passage of a further stream of nitrogen. Coarse particles of $PbSe$ were removed by centrifuging and the lead concentration in the sol estimated by the iodometric method described by Fairhall et al.¹ Using a solution of lead acetate containing 0.4 per cent Pb , approximately 83 per cent of the $PbSe$ -formed was in colloidal form.

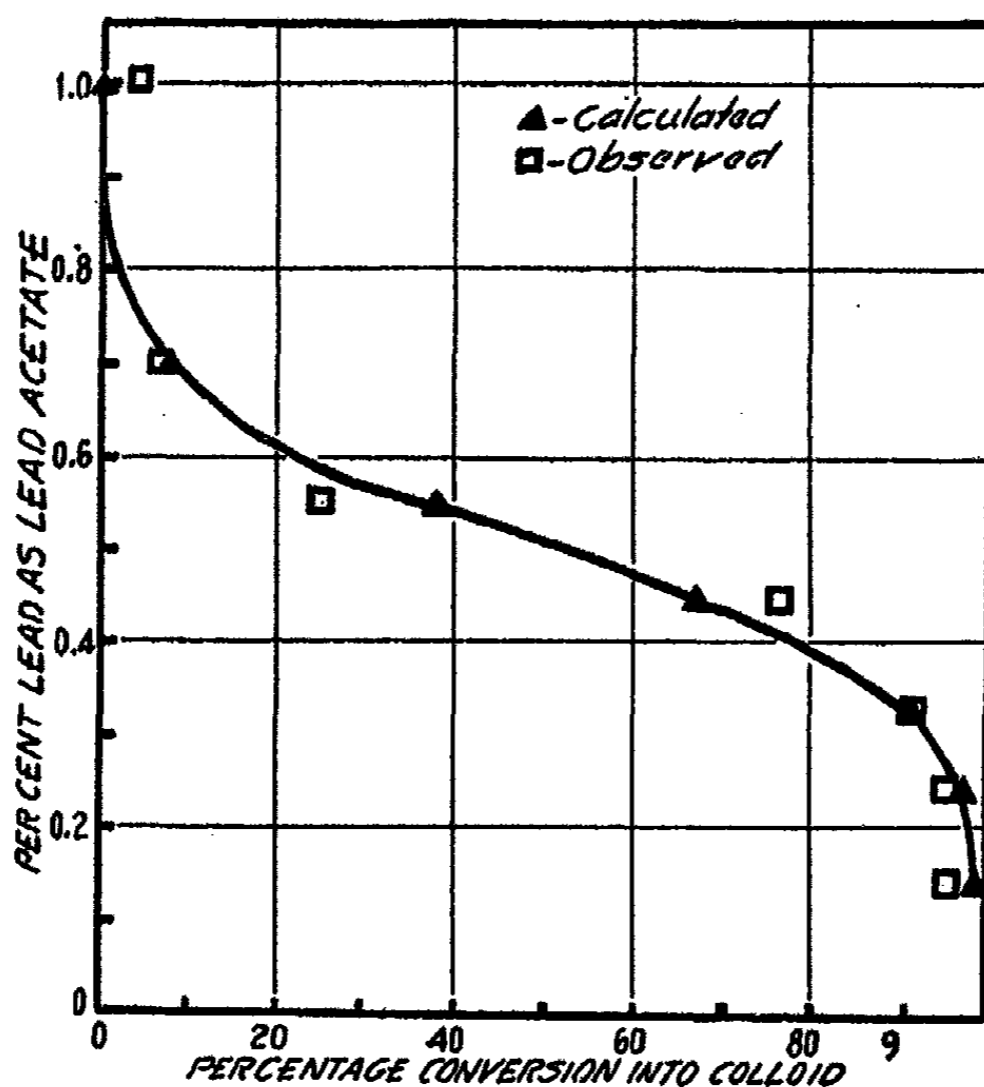


FIG. 1

In thin layers the sol was a clear brownish-yellow, in thick layers it appeared black. The particles were negatively charged and except for a very small amount of initial sedimentation remained stable. The ultra-filtrate contained a negligible amount of ionic lead, and had a pH ca. 7.0.

It was found, on increasing the concentration of the lead acetate solution above a certain range, that the efficiency of the process was markedly decreased, most of the $PbSe$ being in the form of coarse particles which were removed on centrifuging. These results are contained in Table I. In this and other tables the concentration of colloid is that which would be obtained if the sol were made up to the original volume of lead acetate solution. Using uni-

¹ Medicine Monographs, 7, 25 (1926).

form conditions the results for sols 1-4 were reproducible to within 5 per cent, for the remaining sols larger variations were found in the smaller amounts of colloid formed. The curve in Fig. 1 represents the calculated values.

TABLE I

| Sol. | Grms. Lead per 100 cc. | | Per cent conversion into colloid | |
|------|-------------------------|------------------------|----------------------------------|------------|
| | Initial as lead acetate | Final as lead selenide | Observed. | Calculated |
| 1 | 0.15 | 0.143 | 95 | 99 |
| 2 | 0.25 | 0.237 | 95 | 97 |
| 3 | 0.33 | 0.300 | 91 | 91 |
| 4 | 0.45 | 0.342 | 76 | 67 |
| 5 | 0.55 | 0.135 | 25 | 38 |
| 6 | 0.70 | 0.05 | 7 | 8 |
| 7 | 1.0 | 0.04 | 4 | 0 |

In these cases the NaHCO_3 added to neutralise the solution decreased only slightly the amount of colloid which had been formed prior to its addition. (cf. Table V.)

The factors responsible for the decrease in the percentage conversion into colloid would appear to be concerned with the increased concentration of one or more of the following (1) Pb^{++} , (2) CH_3COO^- , (3) H^+ , (4) CH_3COOH . The results contained in Table II show that acetate ion or undissociated acetic acid in sufficient concentration can inhibit colloid formation. The experimental procedure was similar to that described above. No NaHCO_3 was added in 8 and 9 as no acetic acid was formed. Coarse particles of PbSe were removed by centrifuging.

TABLE II

| Sol. | Initial | Final |
|-----------------------------------------------------------------------------------|---------------------------------------------------------------------------------|------------------------------------------------------------|
| | 100 cc. H_2O contain 0.5 gm. gelatin and 1 gm. Lead as | grms. lead (as colloidal PbSe) per 100 cc. |
| 8. Suspended lead hydroxide | | 0.2 |
| 9. Suspended lead hydroxide, together with sodium acetate at a concn. of 0.1 M | | <0.04 |
| | 0.3 gm. Lead as | |
| 10. Lead acetate | | 0.28 |
| 11. Lead acetate, together with acetic acid at a concn. of 0.068 M | | 0.09 |

Expts. 8 and 9 show the inhibiting effect of the acetate ion in a case where the concentration of Pb^{++} was small and no acetic acid was formed. This behaviour of the acetate ion cannot explain alone the decrease in the amount of colloid formed from the more concentrated solutions of lead acetate, as can be

seen from considering the case of a lead acetate solution containing 1.0 per cent Pb (0.048 M.). When 70 per cent of the lead has been converted into PbSe the percentage ionisation of the acetic acid formed (0.068 M.) would be approximately 2 per cent. If therefore acetate ion alone inhibited colloid formation the remaining 30 per cent of the lead should furnish as much colloid as a solution of lead acetate containing 0.3 per cent Pb. This is not the case. Experiments 10 and 11 show however that acetic acid of concentration 0.068 M. can decrease markedly the amount of colloid formed from a solution containing 0.3 per cent Pb. These experiments can give no information, unfortunately, of any effect of lead ion.

In view of these results it was surprising to find that the sols in Table I were not flocculated by lead acetate, sodium acetate or acetic acid in any concentration. The particles of these sols were negatively charged. It was found that actually during the formation (when passing the H_2Se) the charge was positive, presumably by adsorption of H^+ derived from the acetic acid present. The reversal of the sign apparently takes place on the neutralization of the acetic acid by $NaHCO_3$. The positively charged sol before neutralisation (containing excess H_2Se) could also not be flocculated by any concentration of sodium acetate or acetic acid. Since therefore acetate has no effect on the colloid when once formed it seems probable that it influences the process of formation.

The following considerations may be suggested as an explanation.

In the preparation of colloid solutions by condensation methods the governing factors can be considered to be the relative velocities of the formation of nuclei, the growth of the nuclei, and the flocculation of the resulting particles. A large value for the ratio $\frac{\text{velocity of formation of nuclei}}{\text{velocity of growth of nuclei}}$ will result in the formation of small particles and vice-versa. In the present case it seems that the velocity of flocculation of the resulting particles is negligible. It is generally accepted¹ that the velocities of formation and of the growth of the nuclei are independent, and in the case of gold sols this has been demonstrated by Zsigmondy and his co-workers.² It was shown that the presence of different substances during the reduction could alter one process without affecting the other. Hiege has found that ammonium chloride, potassium ferro- and ferri-cyanides inhibit the formation of nuclei without affecting their velocity of growth. This resulted in the formation of coarser particles. The amount of inhibition (measured by the decrease in the number of particles formed) increased with the concentration of added substance and finally at concentrations considerably less than the flocculation values caused the formation of coarse blue sols. Ammonia which did not flocculate a gold sol showed a similar inhibiting effect when present during the formation of the particles of the gold sol.

¹Tammann: *Z. physik. Chem.*, 25, 441 (1898); Freundlich: "Colloid and Capillary Chemistry", p. 327 (English Transl.).

²Zsigmondy: *Z. physik. Chem.*, 56, 65, 77 (1906); Hiege: *Z. anorg. Chem.*, 91, 145 (1915).

In the formation of PbSe it seemed not improbable that a similar effect was present, i.e. acetate ion or acetic acid reduces the velocity of formation of nuclei without affecting the velocity of their growth and in large concentrations (i.e. with large concentrations of lead acetate) cause the nuclei to grow to particles large enough to be removed by centrifuging.

If all the nuclei in any given case grew finally to the same size of particle the transition from complete colloid formation to complete precipitation as the concentration of lead acetate in the initial solution was increased would be abrupt at the concentration corresponding to the formation of particles large enough to be removed by centrifuging. As this is not so it is assumed that in the final state reached (before centrifuging) the sizes or masses of the particles present are governed by a distribution formula,¹ i.e. each mixture contains particles of all probable masses, and that in unit volume the number whose masses lie between m and $m + dm$ is dn , where

$$dn = \frac{4n}{\sqrt{\pi}} \cdot \left(\frac{m}{\sigma}\right)^2 \cdot e^{-(m/\sigma)^2} \cdot d\left(\frac{m}{\sigma}\right) \quad (1)$$

Here σ is the most probable mass of a particle in the particular mixture in question.

The integral of (1) from $m = 0$ to $m = \infty$ equals n , where n is the number of particles of all degrees of dispersion² in unit volume. The mass of the particles lying between m and $m + dm$ is

$$m \cdot dn = dm = \frac{4n\sigma}{\sqrt{\pi}} \cdot \left(\frac{m}{\sigma}\right)^3 \cdot e^{-(m/\sigma)^2} \cdot d\left(\frac{m}{\sigma}\right) \quad (2)$$

The total mass of material present, comprising colloid and non-colloid particles of PbSe is denoted by M and is given by

$$\int_0^{\infty} dm = M = \frac{2n\sigma}{\sqrt{\pi}} \quad (3)$$

When the mixture is centrifuged particles whose mass exceed a certain limit are removed, while all other particles remain in suspension. It is considered that the material remaining in suspension is in colloidal form. The mass of this colloidal material is denoted by M_0 and can be evaluated by integrating (2) between the limits $m = 0$ and $m = m_1$, where m_1 has such a value that particles of mass greater than m_1 are removed on centrifuging. Carrying out this integration

$$\begin{aligned} M_0 &= \frac{4n\sigma}{\sqrt{\pi}} \int_0^{m_1/\sigma} \left(\frac{m}{\sigma}\right)^3 \cdot e^{-(m/\sigma)^2} \cdot d\left(\frac{m}{\sigma}\right) \\ &= \frac{2n\sigma}{\sqrt{\pi}} \left[1 - e^{-(m_1/\sigma)^2} - \left(\frac{m_1}{\sigma}\right)^2 \cdot e^{-(m_1/\sigma)^2} \right] \\ &= M \left[1 - e^{-(m_1/\sigma)^2} - \left(\frac{m_1}{\sigma}\right)^2 \cdot e^{-(m_1/\sigma)^2} \right] \quad (4) \end{aligned}$$

¹ Nordlund: Kolloid-Z., 26, 121 (1920), using Odén's method has determined the distribution of sizes in a mercury sol. He found that the shape of the distribution curve varied with the method of preparation of the sol, sols prepared electrically giving a curve with the most pronounced maximum.

² The concentration of molecular PbSe present is negligible.

As the initial concentration of lead acetate is increased the most probable mass σ of a particle must also increase to account for the decreased fraction (M_0/M) converted into colloid.

For the present purpose the upper limit of the diameter of a colloid particle (mass m_1) is taken as 0.2μ . Assuming that the particles are spherical and of density 8 (approximately the density of lead sulphide) the upper limit of the mass m_1 will be

$$m_1 = \frac{4}{3} \pi r_1^3 \rho \quad \text{where } r_1 = 0.1 \mu \\ = 3.35 \times 10^{-14} \text{ grams.}$$

To evaluate (4) for each initial concentration of lead acetate it is necessary to know σ for each case. This can be obtained from equation (3) if n , the total number of particles (prior to centrifuging) can be determined in each case.

Now the velocity of nuclei formation and hence the number of particles finally formed depends on the concentration of acetate ion or acetic acid present. If therefore a relation could be established from other data between the concentration of inhibiting substance and the number of particles and applied to the present case the required values of σ could be obtained without a knowledge of n . This procedure has been adopted in the following.

As already mentioned, Hiege has determined the total number of gold particles (of all degrees of dispersion since in this case all the particles remained in colloid solution) formed in a reduction mixture containing various concentrations of NH_4Cl . It has been found that Hiege's data fit an empirical equation of the form

$$\log_e n_0/n = ac^b \quad (5)$$

where n_0 is the total number of particles finally formed in the absence of NH_4Cl , n is the total number of particles finally formed in the presence of a concentration c of NH_4Cl (in micromols per litre) and a and b are constants. Table III contains Hiege's data and the values calculated from equation (5).

TABLE III
Flocculation value of $\text{NH}_4\text{Cl} = 27000$ micromols per litre
 $a = 0.0444$; $b = 0.562$

| Concn. NH_4Cl micromols/litre | No. of particles obsvd. in $217 \mu^3$ | No. of particles calculated |
|--------------------------------------------------|-------------------------------------------|--------------------------------|
| 0 | 90 = n_0 | — |
| 38 | 64 | 64 |
| 76 | 52 | 54 |
| 230 | 36 | 35 |
| 380 | 26 | 26 |

In the case of $\text{K}_3\text{Fe}(\text{CN})_6$ where only two values (apart from n_0) are given the exponent b equals 0.61.

The relation found to hold for the results of Hiege is now applied to the present case. It is assumed that the inhibiting effect of acetate ion and acetic

acid is the same,¹ hence they can be considered as one substance with a constant concentration equal to the concentration of acetate ion present at the commencement of the reaction. For the present purpose it must also be assumed that the lead ion is ineffective.

Expressing equation (5) in the form

$$n = n_0 \cdot e^{-ac^b}$$

where n_0 is the number of particles which would be formed if the process could be carried out in the absence of acetate and substituting the above value of n in equation (3) it follows that

$$\sigma = \frac{M\sqrt{\pi}}{2n_0 \cdot e^{-ac^b}} \quad (6)$$

the weight of the n_0 particles being M . The term M/n_0 is the average mass of the particles which would be formed if the process could be carried out in the absence of acetate. It may reasonably be assumed that if twice the amount of lead were used in the absence of any inhibiting substance twice the number of particles would be formed, i.e. M/n_0 is constant. Thus

$$\sigma = k \cdot e^{-ac^b} \quad \text{When } c = 0 \\ k = \sigma_0$$

$$\text{Hence } \log_0 \frac{\sigma}{\sigma_0} = ac^b$$

By a suitable choice of the constant σ_0 , a and b such values of σ were obtained (in terms of the concentrations c of acetate) that on substituting them in equation (4) results for the percentage conversion into colloid were obtained. These have already been given in the final column of Table I. The equation was used in the form

$$\log_0 \frac{\sigma}{\sigma_0} = 4.95 \times 10^{-4} \cdot c^{1.89} \quad (7)$$

where $\sigma_0 = 1.175 \times 10^{-14}$ gram. and c is the total concentration of acetate (acetate ion and acetic acid) in millimols per litre present during the reaction. As should be the case σ_0 (the most probable mass of a particle in the hypothetical case of formation in the absence of acetate) is less than m_1 (3.35×10^{-14} gram.), the upper limit of the mass of a colloid particle of PbSe.

It should be pointed out that these results furnish only indirect support of the theoretical explanation advanced concerning the decreased yield of colloid as the concentration of the initial solution of lead acetate is increased. Given the distribution of particle mass assumed it has been shown that a relation which holds for the results of Hiege on what is believed to be a related phenomenon likewise holds for the experimental results obtained with lead selenide.

From equations (6) and (7) we have already seen that

$$\frac{M\sqrt{\pi}}{2n_0} = \sigma_0 \\ = 1.175 \times 10^{-14} \text{ gram.}$$

¹ Compare sols 9. and 11. in Table II.

$$\begin{aligned} \text{But } \frac{M}{n_0} &= m_0 \\ &= \frac{4}{3} \pi r_0^3 \rho \\ &= \frac{2\sigma_0}{\sqrt{\pi}} \end{aligned}$$

$$\text{Hence } r_0 = 73\mu\mu.$$

M/n_0 is the average mass of the particles which would be formed in the absence of any inhibiting substance, and r_0 is the radius of the average particle. If the upper limit of the radius of a colloid particle had been assumed to be 0.05μ instead of 0.1μ , r_0 would have been $37\mu\mu$. These values are not unreasonable.

In equation (5) relating the number of particles formed to the concentration of inhibiting substance the exponent required, viz:—1.89, is considerably greater than in the case of the gold sol although with PbSe a protective agent is present. A similar equation was used by Marc¹ to express the influence of foreign substances on the velocity of crystallization of supersaturated solutions, the decrease in velocity ($\log v_0/v$) being proportional to the amount adsorbed. In the present case a_0^b can hardly represent adsorption since b is greater than unity. It does not seem probable on general grounds that the effect of foreign substances on nuclei formation would be connected with adsorption.

Alternative Method of Preparation of Lead Selenide Sol

As the above method could not give sols containing more than approx. 0.34 per cent Pb (as PbSe) solid lead carbonate was suspended in the initial solution of lead acetate and gelatin. During the passage of H_2Se , assuming a sufficiently rapid solution of $PbCO_3$ in the acetic acid formed, the concentration of lead acetate should remain constant as long as any $PbCO_3$ remained. By this method the amount of lead present could be increased without increasing the concentration of anion above a value which would result in the inhibition of colloid formation. After the disappearance of the $PbCO_3$ and the passage of excess H_2Se sufficient $N/2 NaHCO_3$ was added to neutralise the acetic acid present. The procedure was then the same as that previously described.

TABLE IV
Grms. lead per 100 cc.

| Sol | Initial mixture | | Final as colloidal lead selenide | Per cent conversion into colloid | Revs. per min. |
|-----|--------------------|----------------------|----------------------------------------|-------------------------------------------|----------------------|
| | as lead acetate | as lead carbonate | | | |
| 12 | 0.35 | 0.31 | 0.09 | 14 | 1300 |
| 13 | 0.35 | 0.31 | 0.246 | 37 | 800 |
| 14 | 0.35 | 0.31 | 0.429 | 65 | 300 |
| 15 | 0.35 | 0.62 | 0.156 | 16 | 1300 |
| 16 | 0.35 | 0.62 | 0.490 | 51 | 300 |

¹ Marc: Z. physik. Chem., 73, 685 (1910).

It was found that a very rapid rate of stirring decreased markedly the amount of colloid formed. The results are given in Table IV, the approximate rates of stirring are in the sixth column. With the slow rate of stirring the disappearance of the PbCO_3 was very slow (requiring approx. 36 hours.)

The expected conversion into colloid was 90 per cent (cf. sol. 3, Table I). In three cases the amount of colloid was less than that which would have been obtained from the lead acetate solution alone, (approximately 0.32 per cent Pb as PbSe). In these three cases it was found that a decrease in the amount of colloid present took place after the addition of the $\text{N}/2 \text{ NaHCO}_3$. In Table V are given the concentration of colloid in sols 13, 14 and 16 before addition of NaHCO_3 (determined by withdrawing a portion of the sol containing excess H_2Se before the addition and centrifuging) and in the neutralised sols after removing H_2Se in the usual way. For comparison similar figures for a lead acetate solution containing no PbCO_3 are given.

TABLE V

| Sol | Initial total grms. lead per 100 cc. | Grms. Pb as colloidal PbSe | | Fraction pptd. by NaHCO_3 | Revs. per min. |
|--------------------|--------------------------------------|-----------------------------------|----------------------------------|------------------------------------|----------------|
| | | Before addtn. of NaHCO_3 | After addtn. of NaHCO_3 | | |
| 13 | 0.66 | 0.415 | 0.246 | 0.41 | 800 |
| 14 | 0.66 | 0.439 | 0.429 | 0.02 | 300 |
| 16 | 0.97 | 0.493 | 0.490 | 0.01 | 300 |
| Lead acetate alone | 0.35 | 0.318 | 0.283 | 0.11 | 800 |
| | 0.35 | 0.323 | 0.315 | 0.03 | 300 |

It will be seen that the fractional decrease in the amount of colloid following the addition of NaHCO_3 is only appreciable in the case of rapid stirring. The influence of stirring on the process of flocculation has been considered by Smoluchowski¹ and found to increase rapidly with the size of the particles, the effect becoming considerable when some of the particles approach macroscopic size. In the experiments with a mixture of lead acetate and carbonate there is a considerable amount of PbSe present in non-colloid form (given by the difference between columns 2 and 3 in Table V) before the addition of NaHCO_3 . This addition reverses the sign of the charge on the colloid particles and it may be assumed that they have a minimum stability at the isoelectric point. It seems not improbable therefore that rapid stirring in the presence of macroscopic particles of PbSe would remove some of the colloid at this point. This is in agreement with the much smaller effect of rapid stirring when lead acetate alone was used (cf. Table V); here the amount of non-colloid PbSe was also small.

¹ Smoluchowski: Z. physik. Chem., 92, 129 (1917), considered a stationary particle and calculated the ratio of the number of particles brought within its sphere of attraction by stirring and by Brownian movement.

The matter appears to be more complex than the above explanation would suggest. It can be seen for example from Table V, column 3, that rapid stirring decreases somewhat the amount of colloid present before NaHCO_3 is added.¹ Further it was found if a rapid rate of stirring was maintained until the addition of NaHCO_3 and slowed down during and after the addition that the decrease in the amount of colloid due to the addition of NaHCO_3 was greater than if the whole process had been conducted at the slower rate of stirring. This is difficult to reconcile with the explanation given in the preceding paragraph. Further investigation is required on these points.

From Table V it can be seen that the yield of colloid was less than the expected value (90 per cent) even before the addition of NaHCO_3 . Because of the slow rate of solution of PbCO_3 in the acetic acid formed, H_2Se accumulated in the mixture before the PbCO_3 had disappeared. Direct reaction of H_2Se with the surface of the particles of PbCO_3 giving lead selenide in non-colloid form would explain the low yield of colloid obtained.

Lead Selenide Sols of High Concentration

It was possible to concentrate a lead selenide sol by long continued boiling. A more convenient method was to add an equal volume of a saturated solution of ammonium sulphate. This precipitated the gelatin in the form of black flocks containing all the lead selenide. On washing free from ammonium sulphate with cold water, the precipitate could be redispersed in warm water to give stable sols of any desired concentration. Owing to the simultaneous increase in the amount of gelatin the more concentrated sols set to stiff gels on cooling.

Summary

I. Two methods for the preparation of lead selenide sols are described using gelatin as a protective agent

- (a) from lead acetate.
- (b) from a mixture of lead acetate and lead carbonate.

2. With the first of these methods the percentage transformation into colloidal lead selenide rapidly decreased as the initial concentration of lead acetate was increased above a certain limit. This effect could be attributed to the presence of acetate ion or acetic acid into which the acetate ion is mainly transformed. As these had no precipitating action on the colloid when once formed it was concluded that the effect was exerted during the process of formation.

3. It is suggested that acetate ion or acetic acid decrease the velocity of formation of nuclei whilst leaving unaltered the velocity of growth of the nuclei. Above a certain concentration the disparity in these velocities is sufficient to produce particles of non-colloid (macroscopic) dimensions. A quantitative treatment has been attempted.

¹ Freundlich and Kroch: *Z. physik. Chem.*, 124, 155 (1926) have studied the coagulation of a CuO sol by stirring alone. They found that this coagulation was not accompanied by any change in the electro-kinetic potential of the particles.

4. With the first method of preparation the rate of stirring had a small effect on the amount of colloid formed. On the other hand with the second method a very rapid rate of stirring decreased markedly the yield of colloid. A provisional explanation is advanced.

5. A method for obtaining a colloidal solution of lead selenide of high concentration is described with gelatin as stabilising agent.

In conclusion the writer wishes to express his best thanks to Professor W. C. M. Lewis, F.R.S. under whose direction this work was carried out, and to Dr. M. Jowett for many valuable suggestions.

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December 8, 1927.*

A CRYOSCOPIC STUDY OF BENZENE SOLUTIONS

BY J. MERRIAM PETERSON¹ WITH WORTH H. RODEBUSH

It has been common knowledge for a long time that some substances, for example acetic acid, appear to have a higher molecular weight (as estimated from vapor pressure lowering) in benzene solutions than in water solutions. Since water has a well known "ionizing" action it may also be suspected of a dissociating action on neutral polymerized molecules and is usually classed as a "dissociating" solvent. In contradistinction benzene is often designated as an "associating" solvent. In view of the known fact that acetic acid has an abnormally high vapor density and that it can be shown theoretically that all molecular weight results even in solution refer to the density of the vapor it may be questioned whether benzene behaves in any way except as an inert solvent.

Another point which requires consideration is that high results for molecular weights obtained by the cryoscopic method might be due to deviations from ideal solution conditions and not to association at all. These questions can best be answered by obtaining complete data for the partial pressures of solvent and solute. Since it is necessary to work in dilute solution in order to apply any of the laws of solution at all, sufficient accuracy cannot be obtained by direct measurement of partial pressures and it is necessary to use the indirect cryoscopic method, which is equivalent to measuring the vapor pressure of the solvent only.

Theoretical

The fundamental law of solutions for changes in composition at constant temperature and pressure is due to Gibbs²

$$m_1 \frac{\partial \bar{F}_1}{\partial m_2} + m_2 \frac{\partial \bar{F}_2}{\partial m_2} = 0 \quad (1)$$

$$\text{where } \bar{F}_1 = \frac{\partial F}{\partial m_1}, \bar{F}_2 = \frac{\partial F}{\partial m_2}$$

Here m_1 and m_2 are the masses in grams of the respective constituents of the solution and F is the total free energy of the solution. If the free energies of the pure constituents are arbitrarily taken as zero then F is the free energy change on mixing. Equation (1) is simply a mathematical statement of the fact that the free energy of mixing depends only on the final amount and composition of the solution. The Duhem-Margules equation is derivable from (1) if the vapors are perfect gases.

The unit of mass is taken as the gram in order that the introduction of the concept of molecular weight may be scrutinized more carefully.

¹ This is an abstract of a thesis submitted by J. M. Peterson in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

² Gibbs: "Scientific Papers," 1, 88 (1906).

If the subscript 1 refers to the solvent we may evaluate the first coefficient of (1) in terms of freezing point lowering. For equilibrium between the solvent in solution and the pure solid solvent we have:

$$\frac{\partial \bar{F}_1}{\partial T} dT = \frac{\partial \bar{F}_1}{\partial T} dT + \frac{\partial \bar{F}_1}{\partial m_2} dm_2 \quad (2)$$

This equation (2) transforms into:

$$\frac{\partial \bar{F}_1}{\partial m_2} = \frac{\Delta H_f}{T_f} \frac{\partial T}{\partial m_2} \quad (3) \text{ since } \frac{\partial F}{\partial T} = -S, \Delta S_f = \frac{\Delta H_f}{T_f}$$

Here ΔH_f is the heat of fusion per gram of the solid solvent into solution. In dilute solution we may assume ΔH_f independent of concentration and neglect the temperature coefficient of \bar{F}_1 . Substituting in (1) which is strictly an isothermal equation.

$$m_1 \frac{\Delta H_f}{T} \frac{\partial T}{\partial m_2} + m_2 \frac{\partial \bar{F}_2}{\partial m_2} = 0 \quad (4)$$

The appearance of dT in an isothermal equation need cause no concern since it represents the amount by which the temperature of the solution would be changed if its freezing point were measured. The best physical measurable quantity to use in expressing the second coefficient of (1) is the partial pressure of the solute. We have

$$m_2 \frac{\partial \bar{F}_2}{\partial m_2} = m_2 V_2 \frac{\partial p_2}{\partial m_2} = \frac{m_2}{\rho} \frac{\partial p_2}{\partial m_2}$$

Where ρ is the density and V_2 the specific volume of the solute vapor. Substituting in (4) we have

$$M_1 \frac{\Delta H_f}{T} \frac{\partial T}{\partial m_2} + \frac{m_2}{\rho} \frac{\partial p_2}{\partial m_2} = 0 \quad (5)$$

So far nothing has been said of molecular weight. The apparent molecular weight M is defined for a gas by the equation

$$M = \frac{\rho R T}{p}$$

where R is expressed in appropriate units. Combining (5) and (6) we have

$$M = - \frac{RT^2}{m_1 \Delta H_f} \left(\frac{\partial \ln p_2}{\partial \ln m_2} \right) \left(\frac{\partial m_2}{\partial T} \right) \quad (7)$$

It is necessary in order to calculate M from freezing point lowering data alone to make some assumption as to the relation of p_2 and m_2 . We may assume that Henry's law $p_2 = kx_2$ where x_2 is the mol fraction of the solute, holds for normal solutes in dilute solution. If the solution is dilute this may be written $p_2 = k.m_2$ and (7) becomes

$$M = - \frac{RT^2}{m_1 \Delta H_f} \frac{\partial m_2}{\partial T} \quad (8)$$

It is common practice to substitute $m_2/\Delta T$ for $\partial m_2/\partial T$ where ΔT is the freezing point lowering but this is only justified if the lowering is a linear function of m_2 . The equation (8) connecting freezing point lowering with molecular weight is not usually given in the exact form and it is important to rec-

ognize its exact significance. Provided the assumption of Henry's law is justified, we can calculate the *apparent molecular weight* as defined by eq. (6) in the vapor state, for the solute. The vapor is not assumed to be a perfect gas. If Henry's law does not hold the calculations will be in error. It is important to note that the proper value of $\partial m_2/\partial T$ must be used for a given concentration. It cannot be emphasized too strongly that a molecular weight, as determined in solution by freezing point lowering, depends only upon the vapor density of the solute and not upon the vapor density of the solvent.¹ Several questions are at once suggested by the above statement. What does a molecular weight mean for a nonvolatile solute, and how can a solute have different molecular weights in different solutions? A molecular weight determination for a nonvolatile solute gives us a hypothetical vapor density. If a solute does not give the same molecular weight in different solutions then one of two things must be true. Either the solute has a variable molecular weight in the vapor state depending on the pressure e. g. acetic acid vapor, or the assumption of Henry's law is not justified. If Henry's law does hold and a solute shows different molecular weights in different solvents at the same concentration the partial pressures over the different solutions must be different to account for the variable vapor density indicated. This may imply a different state of association in the various solvents but it does not give any exact information.

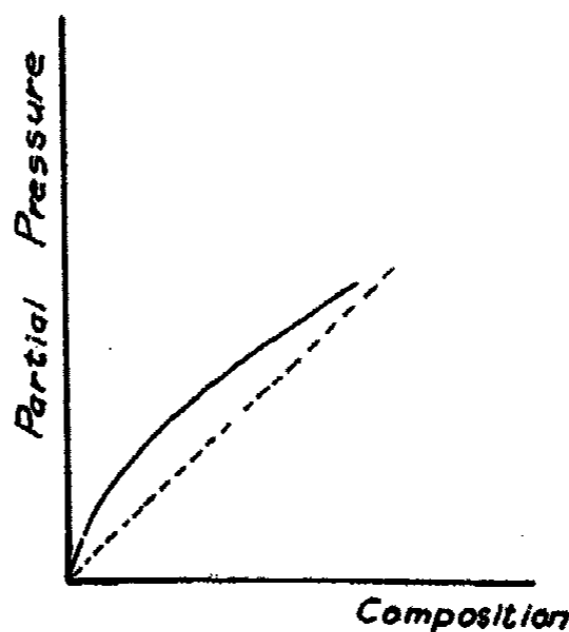


FIG. 1

It is impossible to avoid some uncertainty as to the amount of error involved in the assumption of Henry's law. Even in the case where the freezing point lowering is a linear function of the concentration so that $\partial m/\partial T$ is constant it does not follow that Henry's law holds, unless the apparent molecular weight of the solute in the vapor state is likewise known to be independent of concentration. In general, Henry's law cannot hold for an associated solute. At the extremes of concentration however, where the dissociation is either slight or nearly complete Henry's law may hold. In solutions of appreciable concentration the deviation from Henry's law will depend, in the simple cases at least, on the deviation of the Henry's law constant from the ideal solution constant.¹ This will be evident from Fig. 1 where the dotted line indicates the ideal solution partial pressure and the heavy lines the partial pressures for typical solutions. For positive deviations at any point $\partial p_2/\partial m_2$ will be less than p_2/m_2 , while the reverse will be true for negative deviations. We have the identity

¹ Contrast with J. Kendall: J. Am. Chem. Soc., 43, 1391 (1921).

$$\frac{\partial \ln p_2}{\partial \ln m_2} = \frac{\partial p_2 / \partial m_2}{p_2 / m_2}$$

If $\partial p_2 / \partial m_2 < p_2 / m_2$ then the use of the simplified form (8) will lead to too large a value for the molecular weight. For positive deviations from ideal solutions then we may expect too large a value of the molecular weight in all except extremely dilute solutions. A negative deviation will produce the reverse effect. These theoretical considerations will be referred to later in connection with the data obtained in this work.

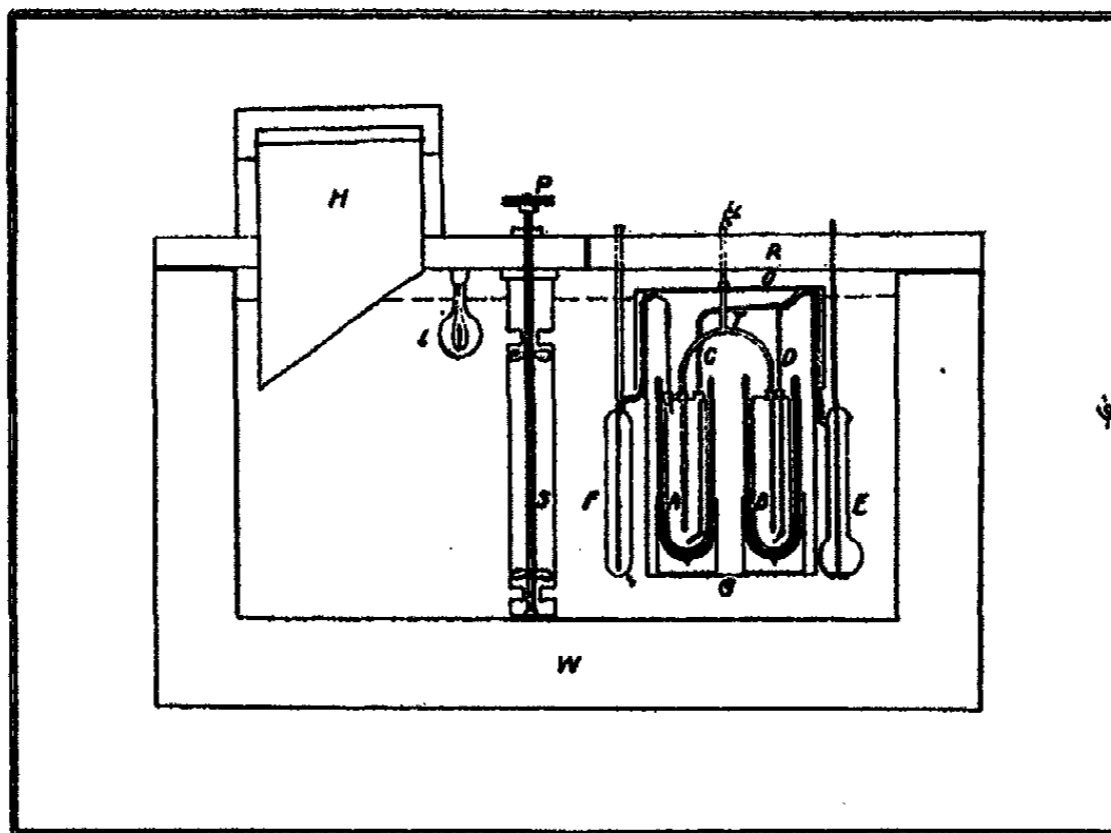


FIG. 2

Experimental

A number of the earlier workers with the cryoscopic method obtained data on benzene solutions. Prominent among these are Raoult,¹ Beckman,² Auwers,³ Paternò,⁴ and Rozsa.⁵ All of this work, however, was done with mercury thermometers and comparatively crude apparatus, so that a high percentage accuracy could not be obtained in dilute solution where Henry's law may be assumed to hold. In the work described in this paper the greatest lowering measured was 0.257°C.

Apparatus: The apparatus consisted essentially of two freezing point bulbs A and B Fig. 2 which were placed in Dewar tubes. In the top of the bulbs were openings for the insertion of the thermocouple, air bubbling tube, pipette, etc. These openings were made tight by perforated corks which had been extracted with benzene. This part of the apparatus was enclosed in a

¹ Raoult: *Ann. Chim. Phys.*, 2, 66 (1884).

² Beckman: *Z. physik Chem.*, 2, 715 (1888).

³ Auwers: *Z., physik Chem.*, 42, 513 (1903).

⁴ Paternò: *Ber.*, 22, 1430 (1889).

⁵ Rozsa: *Z. Electrochemie*, 17, 934 (1911).

copper can which was nearly submerged in a water thermostat. The cover of heavy sheet copper was above the water level but this has been shown to give satisfactory temperature equilibrium.¹ The thermostat was heavily insulated, cooled by the ice box H and heated by the lamp L. A conventional type of mercury regulator was used and no difficulty was experienced in maintaining any temperature between 5° and 25°C with variations less than 0.01°.

The thermocouple was a ten-junction copper-constantan couple of resistance 54.2 ohms and a calibrated e.m.f. of 396.6 microvolts per degree at the freezing point of benzene. The e.m.f. was read on the self-calibrating potentiometer devised by Rodebush,² with a precision of 0.02-0.03 microvolt.

Experimental Procedure

The apparatus was designed originally with the expectation of following the experimental procedure used by Hovorka and Rodebush on dilute water solutions. Surprising difficulties were met with however because of the peculiar waxy nature of solid benzene. It cannot be broken up into conveniently sized particles, as can ice, nor can it be handled in contact with the air because of the absorption of moisture which produces a marked change in the freezing point. In order to get a satisfactory temperature equilibrium in freezing solutions it is necessary to have a mush of fine solid particles in contact with liquid. The ordinary laboratory method of producing this mush by supercooling did not produce enough of the solid to cover the thermocouple to a satisfactory height. This method was actually used with some success, by supercooling the benzene very markedly and it is probably the simplest and best method, but one day it suddenly became impossible to supercool benzene more than a degree in the laboratory and the method had to be abandoned. This sort of experience is of course a common occurrence in crystallization work.

It became necessary therefore to devise a new procedure of obtaining a mush of solid benzene. The method finally adopted was as follows:

The freezing point tubes were filled with pure benzene, stoppered, and placed in a beaker of ice water until a thin layer of solid had formed on the sides of the tube. The tube was then removed and warmed slightly with the hand whereupon, on shaking, small particles of solid benzene would break loose from the sides and settle to the bottom of the tube. By repeating this process a satisfactory amount of solid free from contamination was produced. The temperature equilibrium obtained was not as perfect as can be had with ice and water but it was usually constant within 0.001°.

When a sufficient amount of solid had been obtained in two tubes they were placed in the thermostat and the thermocouple and the various connecting tubes inserted. The tube B served as the standard temperature bath for the thermocouple while the benzene was withdrawn from A through the bubbling tube C. The solid benzene in A was rinsed free of pure benzene by introducing small quantities of the solution from F and withdrawing it through

¹ White: J. Am. Chem. Soc., 48, 1149 (1926).

² Hovorka and Rodebush: J. Am. Chem. Soc., 47, 1614 (1925).

C. When this had been repeated several times the tube A was filled with solution and equilibrium obtained by bubbling purified air saturated with benzene vapor through both tubes. All the solutions were handled out of contact with the air or any possible source of contamination. The solutions were made up by direct weighing. The small amounts of solute were sealed in glass bulbs for weighing and the bulb broken beneath the surface of a weighed amount of benzene, to make up the solution.

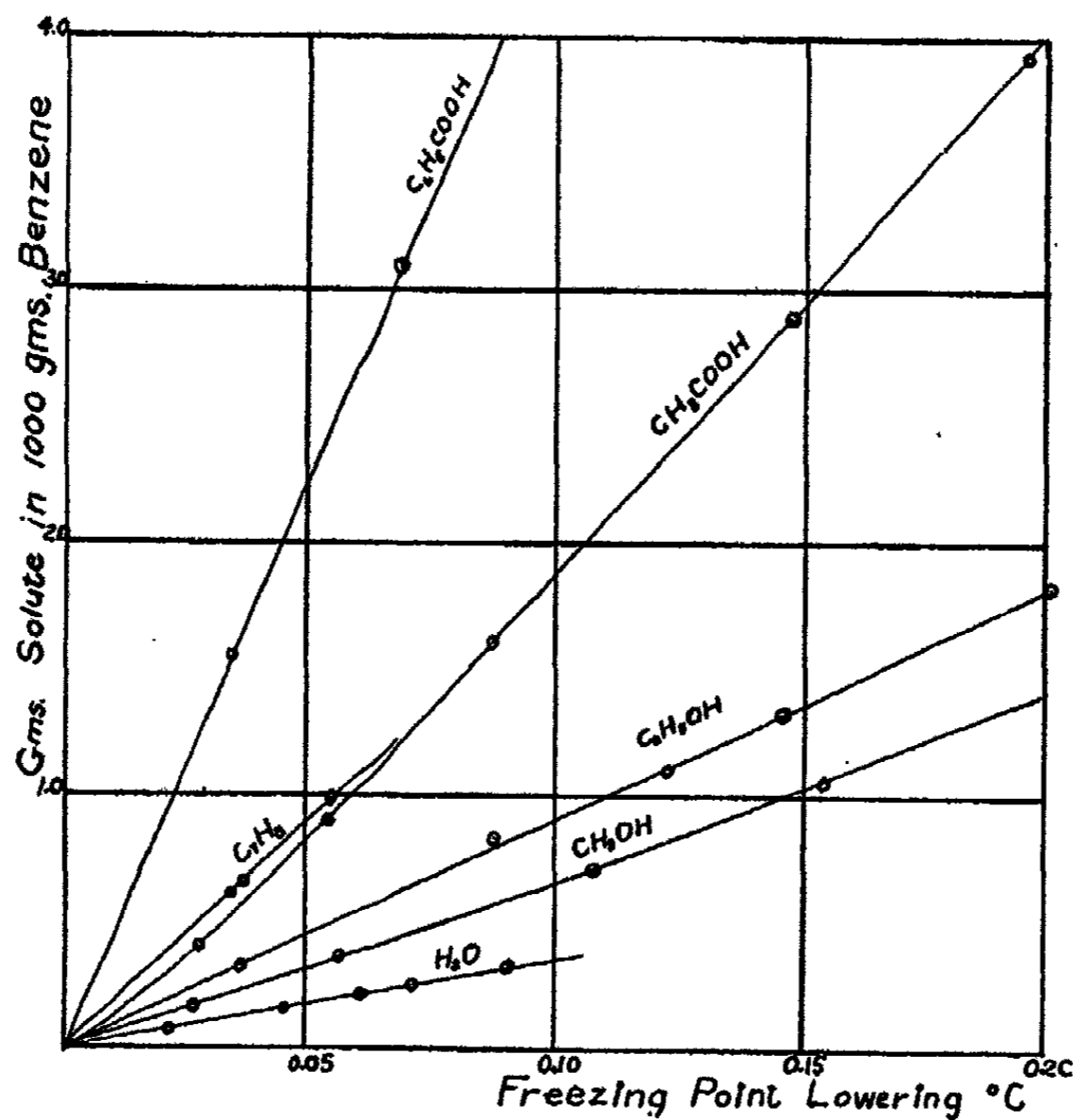


FIG. 3

Preparation of Materials: Benzene. Very pure benzene may be obtained because of the possibility of freeing it from most of its impurities by fractional crystallization or freezing. Thiophene, it is true, cannot be separated in this way but this impurity can easily be removed chemically. On the other hand, paraffin hydrocarbons, olefins, acetone and most other impurities are quickly eliminated from the successive crop of crystals.

Mallinckrodt's best grade of thiophene-free, pure benzene was used. This was fractionally crystallized 5 times discarding about one-tenth of it each time. It was then fractionally distilled twice, using a tall, efficient, fractionating column, the last time from phosphorus pentoxide directly into the freezing point tubes. The distilling apparatus as well as the tubes were thoroughly dried, by a stream of dry air, immediately before use and were protected during the distillation by a phosphorus pentoxide tube. The first benzene dis-

tilling over was never used and the last portion in the flask was never distilled. The boiling point of the benzene used varied less than .02 degree C. Further treatment appeared to have no effect upon the freezing point.

Acetic acid. Kahlbaum's acetic acid labeled "100 percent" was used. This was recrystallized 5 times and fractionally distilled from a small amount of phosphorus pentoxide. Only the middle fraction was collected for use. Altho the very constant reading of the thermometer would not indicate any acetic anhydride in the distillate, this possibility was eliminated by a further purification by freezing.

Water. "Conductivity" water was used.

Methyl alcohol. A c.p. grade of methyl alcohol was used which was dried with magnesium methylate and fractionally distilled.

Ethyl alcohol. Absolute ethyl alcohol was further dried with magnesium ethylate and fractionated.

Benzoic acid. The purity of the benzoic acid used was certified by the Bureau of Standards. It was recrystallized and dried in a vacuum desiccator.

TABLE I

A = gms. solute in 1000 gms. benzene

B = freezing point lowering in centigrade degrees

| A | B | A | B |
|----------------|--------|--------------|--------|
| Methyl Alcohol | | Toluene | |
| 0.168 | 0.0268 | 0.610 | 0.0338 |
| 0.364 | 0.0570 | 0.658 | 0.0366 |
| 0.710 | 0.1078 | 0.981 | 0.0549 |
| 1.062 | 0.1546 | | |
| 1.681 | 0.2342 | | |
| Ethyl Alcohol | | Acetic Acid | |
| 0.322 | 0.0364 | 0.201 | 0.0156 |
| 0.803 | 0.0878 | 0.399 | 0.0277 |
| 1.089 | 0.1223 | 0.805 | 0.0539 |
| 1.327 | 0.1459 | 1.611 | 0.0875 |
| 1.830 | 0.2013 | 2.894 | 0.1472 |
| 2.262 | 0.2442 | 3.923 | 0.1957 |
| | | 4.452 | 0.2199 |
| | | 4.897 | 0.2401 |
| Water | | Benzoic Acid | |
| 0.074 | 0.0214 | 1.557 | .0342 |
| 0.159 | 0.0450 | 3.094 | .0683 |
| 0.021 | 0.0606 | 4.802 | 0.1060 |
| 0.248 | 0.0716 | 8.774 | 0.1897 |
| 0.320 | 0.0907 | 11.236 | 0.2402 |
| 0.382 | .0990 | | |
| 0.5 | .0986 | | |
| 1.0 | .0984 | | |

Toluene. The toluene was prepared by the acid hydrolysis of p-tolyl sulfonic acid. The resulting product was fractionated.

Results: The results are given in Table I and are shown graphically in Fig. 3. It will be noted that the freezing point depression appears to be a linear function of the weight of solute per 1000 gms. of benzene for all of the substances except acetic acid and methyl alcohol. The results in the case of ethyl alcohol are not sufficiently consistent to determine absolutely that no curvature exists but a straight line fits the data as well as any curve that could be drawn. In the case of the other solutes there can be no doubt, in dilute solution at least, as to the linear relation. There appear to be no data in the literature of high accuracy for very dilute solutions of the substances we have investigated except in the case of water. Richards, Carver and Schumb¹ determined the freezing-point depression of benzene saturated with water to be 0.095°C which is close to our value of 0.0987°C. We find by extrapolation that the solubility of water at the freezing point is 0.35 gm. per 1000 gms. of benzene.

The toluene solutions were studied with the special purpose of determining the so called "molal freezing point" constant for benzene. Since even in the case of Henry's law can not be assumed except as a limiting law results were obtained only in very dilute solutions. The value obtained in this way is 5.11 but the experimental error makes the last figure uncertain. The value calculated by equation (8) from the heat of fusion of benzene is 5.07 but the most probable heat of fusion 30.4 cal/gm as estimated from numerous determinations in the literature must be uncertain by $\frac{1}{2}$ percent.² The value which we shall adopt 5.10 appears to give satisfactory values for the apparent molecular weights at infinite dilution for the various solutes and is probably not in error by more than one percent.

In Fig. 4 the values of $\partial m/\partial T$ for the various solutes are plotted against the freezing point lowering. The values of $\partial m/\partial T$ are obtained by graphical methods from the curves of Fig. II and are of course not of high accuracy except in the cases where the curve is linear. Since, assuming Henry's law, the apparent molecular weight is $5.1 \times \partial m/\partial T$ this quantity is also shown on the left side of Fig. 3. It should be noted in advance that an apparent molecular weight greater than the formula weight is easily accounted for as due, either to association or positive deviation from the ideal solution law, while a value less than the formula weight probably means error in the value estimated for $\partial m/\partial T$ since negative deviations from the ideal solution law are not probable. In the case of water and ethyl alcohol the apparent molecular weights are independent of concentration and equal respectively to 18.1 and 46.4 indicating no appreciable association of the vapors. Some association is indicated in the case of methyl alcohol and the limiting value of 31.1 may be due to error or to one of the causes noted above. The case of acetic acid is that of a typical associated vapor. The value of 59 at infinite dilution is probably too low because of error in extrapolation. Undoubtedly acetic acid vapor is completely depolymerized at low pressures and approaches the double for-

¹ Richards, Carver and Schumb: J. Am. Chem. Soc., 41, 2019 (1919).

² See Landolt-Börnstein-Roth: "Tabellen."

mula at high pressures. Our measurements cover practically the entire range from complete dissociation to complete association but it is only at the lower limit of concentrated that Henry's law may be assumed to be anything more than a rough approximation. Molecular weights calculated over the rest of

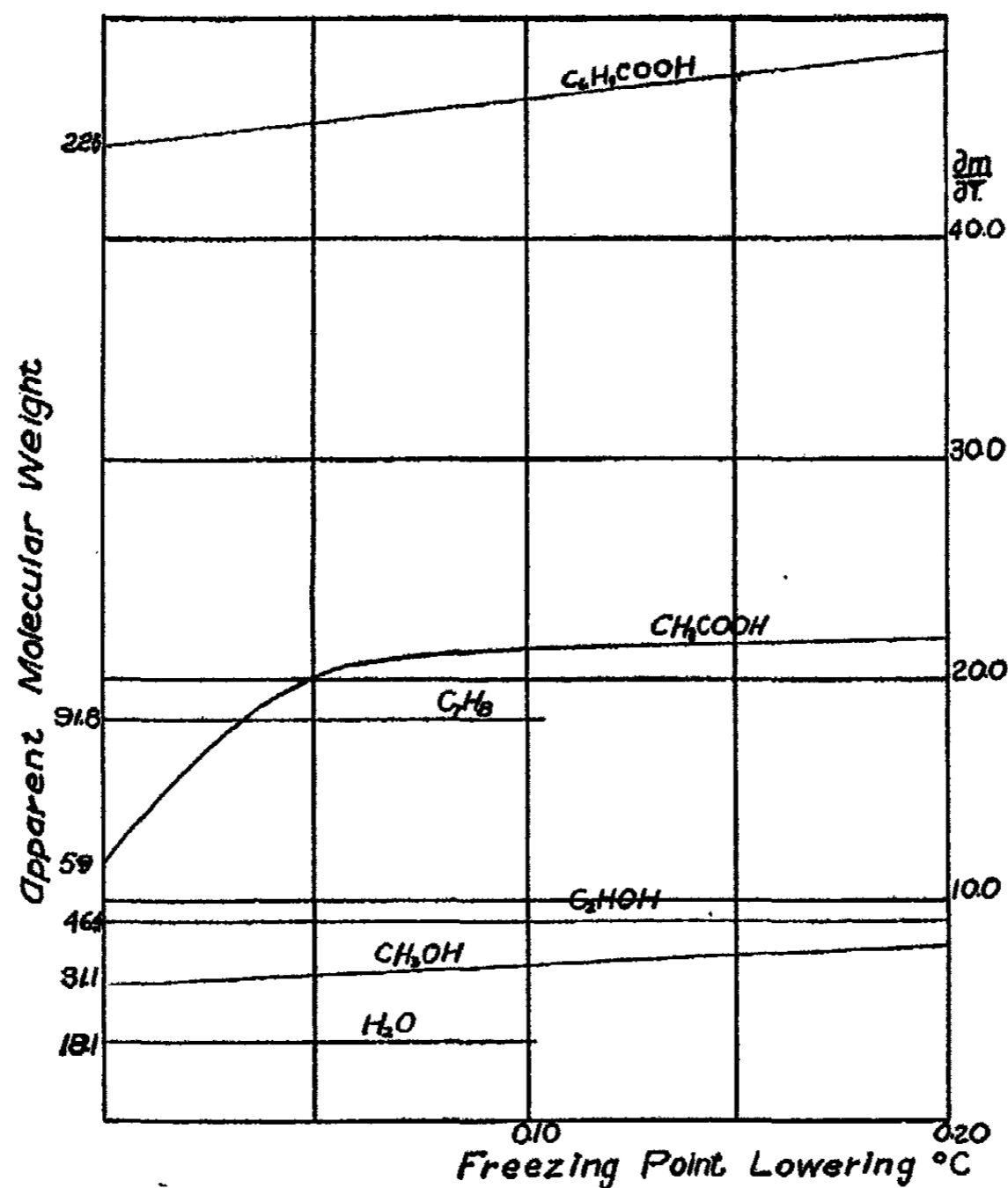


FIG. 4

the range measurements must be regarded as approximations only. The case of benzoic acid is somewhat different. At the higher concentrations the vapor density corresponds to the double formula or even a greater degree of association, while the measurements have not been carried to sufficiently low concentrations to show the complete dissociation as in the case of acetic acid. The extrapolation to zero concentration is without significance. Henry's law cannot be assumed to hold in any part of the measured range except as a rough approximation. In view of the small vapor pressure of benzoic acid it is seen that the polymerized molecule of benzoic acid is a far more stable affair than the polymerized acetic acid molecule.

From the foregoing considerations one may draw the conclusion that for all of the solutes investigated, except benzoic acid, Henry's law holds at least in the more dilute solutions; and that where the freezing point depression indicates polymerization an abnormal vapor density actually exists. The latter conclusion is, as shown in the beginning of this paper by thermodynamic reasoning, a necessary consequence if the first is true.

Summary

An exact equation has been derived from thermodynamics, which relates the freezing point depression of a dilute solution to the vapor density of the solute.

Data are given for the freezing point lowerings of dilute benzene solutions for a number of solutes.

The vapor densities of the solutes are calculated from the freezing point data.

Urbana, Illinois.

THE SYNTHESIS OF WATER OVER NICKEL AND COPPER CATALYSTS. THE MIXTURE EFFECT AND PROMOTER ACTION

BY FRANCIS E. SMITH

It has been shown in a previous paper¹ that the mechanism of the catalytic synthesis of water vapor is essentially the same for both nickel and copper catalysts. Starting in each case with metal prepared by reducing the oxide in the form of porous granules, the results showed that the catalytic reaction consists of two separate stages. The first, or initial, stage is characterized by a relatively high rate of synthesis, a relatively low, or zero, rate of leakage of free oxygen gas past the catalyst, and the gradual covering of the reduced metal by a layer of oxide. The spreading of this oxide over the catalyst can be followed visually in the case of copper, and with both metals by the temperature effects produced at the oxide-metal boundary. The second stage in the catalytic reaction follows the covering of the catalyst by this stable oxide. It is characterized by a lower rate of synthesis, a much higher rate of oxygen leakage, an extremely slow rate of formation of further oxide, and the absence of further temperature effects. The separation of the two stages is less distinct with copper than with nickel, but the general similarity of behavior in the two cases is quite evident.

It should be emphasized that only in the second stage is there what may be called "true" catalysis, and that the initial stage is really "catalysis with destruction of the catalyst." Whether this destruction is necessary to the synthesis in the first stage, or whether it is the result of a side reaction which plays little or no part in the catalysis, was not definitely shown by the then existing data, but the latter hypothesis seemed the more probable.

The interpretation given these experimental results was that the catalytic mechanism involved a fast reaction between an "indefinite" oxide and hydrogen, and that this was inhibited by the covering of the catalyst by the layer of oxide. This interpretation can be stated equally well by saying that it involves the alternate, or more probably simultaneous, formation of an "indefinite" oxide and its reaction with hydrogen. In view of the proved inhibiting action of free gaseous oxygen on the reduction, but little importance was attached to the possibility of a mechanism involving alternate reduction of the stable oxide and reoxidation of the metal surface thus exposed, a mechanism first proposed by Pease and Taylor² for the catalysis with copper. These authors postulated, on the basis of preliminary observations, an entirely different mechanism for the catalysis with nickel. Our results showed, however, that the behavior of these metals is essentially the same, and that the most probable mechanism for one must be that for the other. In the

¹ Larson and Smith: *J. Am. Chem. Soc.*, 47, 346 (1925).

² Pease and Taylor: *J. Am. Chem. Soc.*, 44, 1637 (1922).

Fourth Report of the Committee on Contact Catalysis,¹ the interpretation of the results for both nickel and copper given in our paper is accepted by Taylor in preference to the mechanism involving the stable oxide.

Benton and Emmett,² however, in an article on the water synthesis over nickel, attempt to show that the stable oxide is an essential step in the catalytic mechanism. While there is no disagreement regarding the experimental facts, the conclusions reached by these authors appear to be unjustified. Their interpretation will be discussed in a later section.

The present paper gives the results of further experiments with pure nickel and copper catalysts, and extends the investigation into the field of mixed and promoted catalysts. Evidence is presented to show that the physical nature of the catalyst surface, as well as its chemical properties, is of primary importance in determining the catalytic activity. The results are, in general, consistent with the theory of the catalytic mechanism given in the first paper, and are presented as further support for it.

Preparation of Catalytic Material

All the catalysts used in the present work, with but one exception, were prepared by reduction in hydrogen of the precipitated hydroxides, following the procedure described in the first paper.³ These precipitated hydroxides, which were in the form of porous granules of 8-14 mesh size, varied somewhat in hardness. In the copper-nickel series there was a gradual increase in hardness from pure copper to pure nickel. The copper-alumina was more firm than the corresponding copper, and pure nickel was firmer than copper-alumina. Of the two precipitated copper hydroxides, that in the copper-nickel series was less hard than that in the copper-alumina.

The one exception to the method of preparation by precipitation was in the case of a fused copper oxide.⁴ Electrolytic copper wire was roasted in a rotating furnace through which a current of air was passed. The resulting oxide was fused in an electrically heated furnace in the presence of oxygen. After cooling, the fused mass was crushed and screened to 8-14 mesh. The oxide granules were hard and dense, and were black in color. Analysis showed a copper content of 87.3 per cent., corresponding to the composition: 19.6 per cent. cupric, and 80.4 per cent. cuprous oxide.

The preliminary treatment and reduction of the catalyst material were carried out *in situ* as described in the first paper. The reduction at 218° was continued, as in the previous work, until analysis of the effluent gas by passage thru phosphorus pentoxide weighing tubes, showed that it contained less than 0.1 mg. of water per 6 liters of gas. Evidence that the reduction of the porous oxides was complete is presented in the next paragraph.

Samples of the catalysts, after reduction at 218° and operation (as described later) at temperatures not exceeding 184°, were heated at 444° in a

¹ Taylor: *J. Phys. Chem.*, 30, 157-8 (1926).

² Benton and Emmett: *J. Am. Chem. Soc.*, 48, 632 (1926).

³ Larson and Smith: *J. Am. Chem. Soc.*, 47, 346 (1925).

⁴ This oxide was prepared at the Fixed Nitrogen Research Laboratory, Washington, D.C.

stream of pure hydrogen for one-half hour. Additional water was obtained in only two cases,—fused copper¹ gave 31.4 mg., and copper-alumina, 3.6 mg. In the latter case, the water was undoubtedly derived from hydrated aluminum oxide, since dehydration of this oxide is not complete at 218°. The fused copper oxide was not completely reduced at 218°, and fused nickel oxide would no doubt have behaved similarly. This behavior is easily explained as due to the non-porous nature of the granules, which prevented ready access of hydrogen to the interior oxide. However, the evidence is conclusive that the porous oxides obtained from precipitated hydroxides can be completely reduced by hydrogen at temperatures as low as 218°.

Table I gives the compositions by weight of the reduced catalysts, as calculated from analyses of the original granules. No account is taken of the presence of some oxide in catalyst No. 3, the fused copper, nor of the presence of water in combination with alumina in catalyst No. 2b.

TABLE I
Compositions of the Catalysts, per cent. by weight

| Catalyst | Copper | Nickel | Alumina |
|-------------------|--------|--------|---------|
| 1a Copper | 100 | — | — |
| 1b Copper-Nickel | 88.2 | 11.8 | — |
| 1c Nickel-copper | 25.5 | 75.5 | — |
| 1d Nickel | — | 100 | — |
| 2a Copper | 100 | — | — |
| 2b Copper-alumina | 95.5 | — | 4.5 |
| 3 Fused copper | 100 | — | — |

The amounts of shrinkage of the different oxides during the preliminary treatment and reduction varied within rather wide limits. The precipitated coppers shrank most of all, while pure nickel, fused copper, and copper-alumina shrank least. The copper-nickel mixtures were intermediate between pure copper and pure nickel in this respect. The volumes of freshly reduced catalyst were in general about 3 cc. This smaller volume as compared with that used in the previous work (7-9 cc.) was found desirable in order to decrease the lengths of the runs, and in particular the lengths of the initial stage in the catalysis. With continued use some further decrease in volume was usually observed, but at no time was the amount of catalyst less than 2 cc.

Experimental Part

The apparatus, shown diagrammatically in Fig. 1, was similar to that used in the previous work, except that no provision for humidification of the gases was made. The final drying of the gases was effected by their passage thru tubes of phosphorus pentoxide and fused potassium hydroxide. Oxygen was added to the hydrogen from the electrolytic cell (1), and its concentration was

¹The expression "fused copper" will be used to designate the catalyst prepared by reduction of fused copper oxide. Similarly, "precipitated copper" will mean a catalyst prepared from the precipitated hydroxide. When no distinguishing adjective is used in this connection, the precipitated catalyst will be meant.

kept constant at 10 mg. water-equivalent per 5 minute interval. The flow of hydrogen was 100 cc. per minute (0° , 760 mm.). Weighings of the water in the effluent gas were made at suitable intervals, and when desired, the rate of oxygen leakage was determined as in the previous work. Further details are given in the first paper.

Some of the runs were continued over a period of many days, and the catalyst had to be left standing over night. It was found possible to do this with little or no reduction of the stable oxide, if the completely oxidized catalyst was cooled rapidly to room temperature and shut off under a slight excess pressure of the mixed hydrogen-oxygen gases. The following morning the

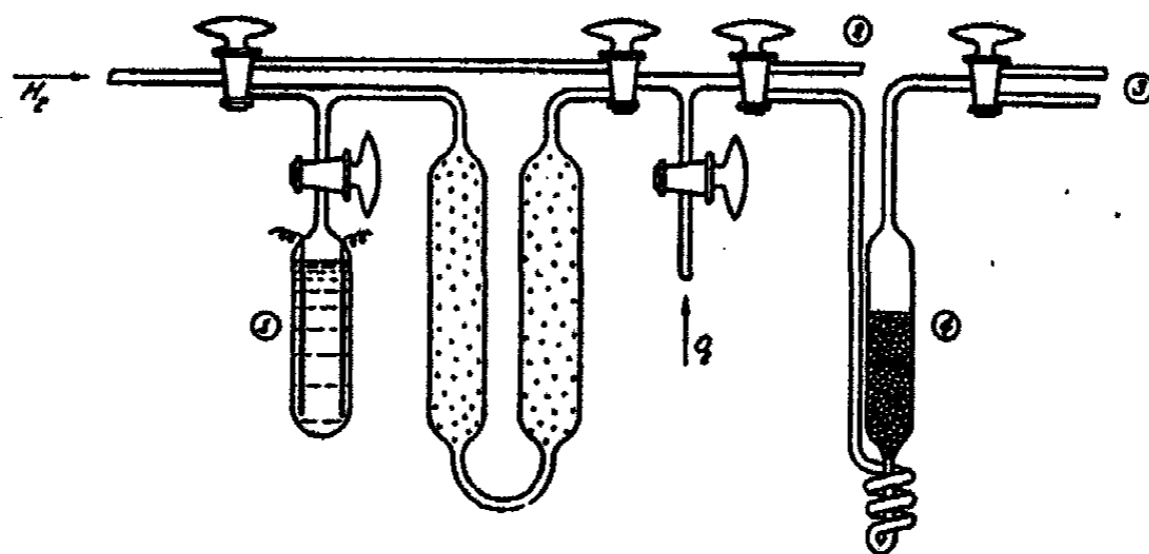


FIG. 1
Apparatus

catalyst was flushed at room temperature with the mixed gases for about 10 minutes, and was then heated rapidly to the temperature used the previous day. In most cases but little water vapor had accumulated during the overnight period, and there was no great amount formed on heating. It was thus possible to make "continuous" runs without reduction of the oxide. When a run had been completed, the oxide present on the catalyst was determined by shutting off the oxygen and passing pure hydrogen over the catalyst, final reduction being carried out in all cases at 184° . Subsequent heating at higher temperatures up to 444° , as already described, showed that the oxide formed during catalysis can be completely removed in this way.

Experimental Results

Typical results of the present series of experiments are shown in Figs. 2 and 3. Fig. 2 shows the character of the initial stage of the catalysts for the different catalysts, while in Fig. 3 efficiencies of conversion in the final steady state are plotted against temperature.

As the curves of Fig. 2 show, there are apparently (but, as will be shown immediately, not really) two distinct types of initial reaction, one characterized by a rather long, flat maximum and a rapid decrease in the rate of synthesis, and the other by a much shorter maximum with a more gradual rate of decrease. The catalysts which may be considered as being of the long maxi-

mum type are pure nickel, nickel-copper, and copper-alumina. Those having short maxima are the precipitated coppers, fused copper, and copper-nickel. In this respect, as in others to be mentioned later, there is no specific "mixture" effect in the copper-nickel series. In general the properties varied gradually from pure copper to pure nickel.

That there is no essential difference between the two types of curves is shown by an examination of the results at different temperatures. In the case of each catalyst there is evidence of a transition, with increasing temperature, from the short maximum to the long continued maximum type, and this evi-

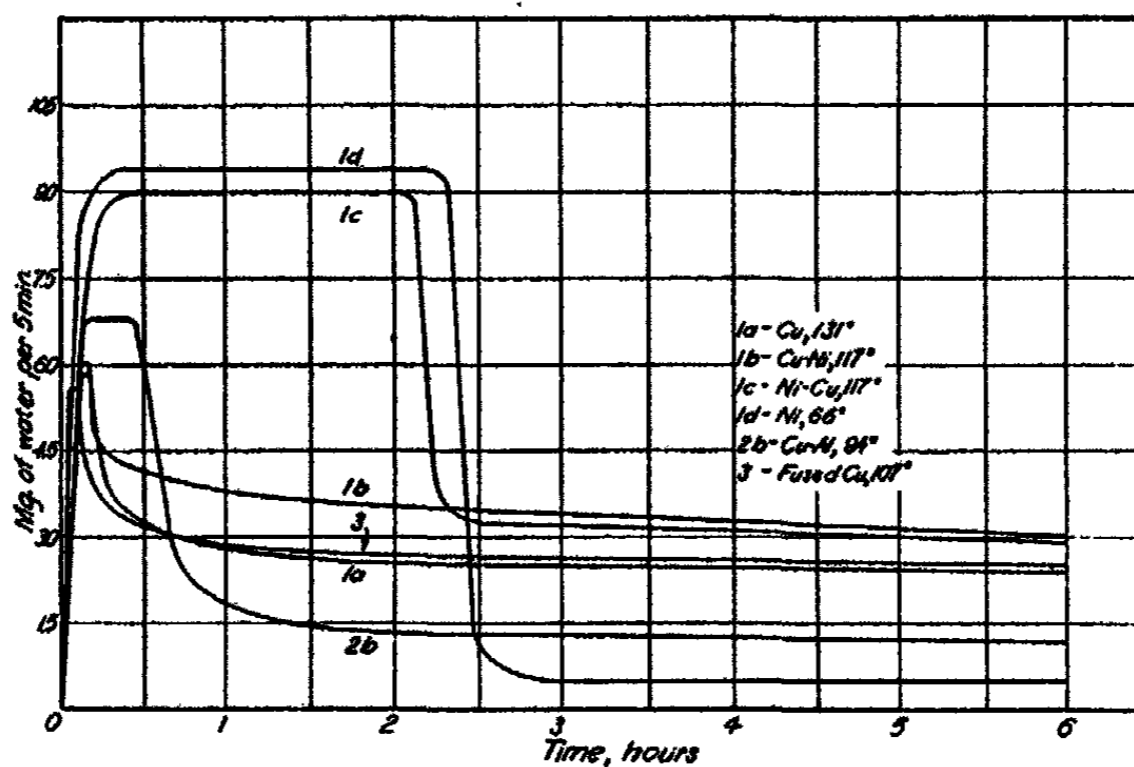


FIG. 2
Rates of water formation in typical runs

dence is conclusive in two instances. Thus when precipitated copper, catalyst No. 1a, which gave curves of the short maximum type at temperatures from 78° to 156°, was run at 164°, it gave a maximum of 9.9 mg. of water per 5 minutes lasting more than four hours, and then showed a rather rapid decrease to 7.0 mg. at the final steady state. Also in the case of copper-alumina, No. 2b, at 94° the curve (shown in Fig. 2) is evidently intermediate in character, since the flat maximum at 6.8 mg. lasts less than half an hour. At a lower temperature, 79°, there was a sharp maximum, and at a higher temperature, 107°, the rate of water formation increased slowly from 9.2 mg. per 5 min. at the end of the first hour to 9.8 mg. at the end of 15 hours. A similar increase in the rate of synthesis during the initial stage was observed for the other catalysts of this type, altho to a lesser degree.

In all cases in which there was a continued maximum, the oxygen leakage was zero up to the point at which the decrease in efficiency took place. Simultaneously with the beginning of this decrease, the oxygen leakage increased to a point such that the sum of the synthesis and leakage accounted for all the oxygen entering the catalyst chamber. The rate of further oxide formation is therefore not measurable by difference.

It should be pointed out at this time that it is not strictly correct to say that the efficiency of the catalyst during the initial stage, when there is no oxygen leakage, is anything less than 100 per cent. There are present under these conditions two competing reactions, one forming oxide which remains on the catalyst, and the other forming water. If, for example, one-tenth of the oxygen striking the catalyst is permanently fixed as oxide, only nine-tenths is left for the catalytic reaction. If the catalyst converts this completely to water, it is doing all that can be expected of it and is in the true

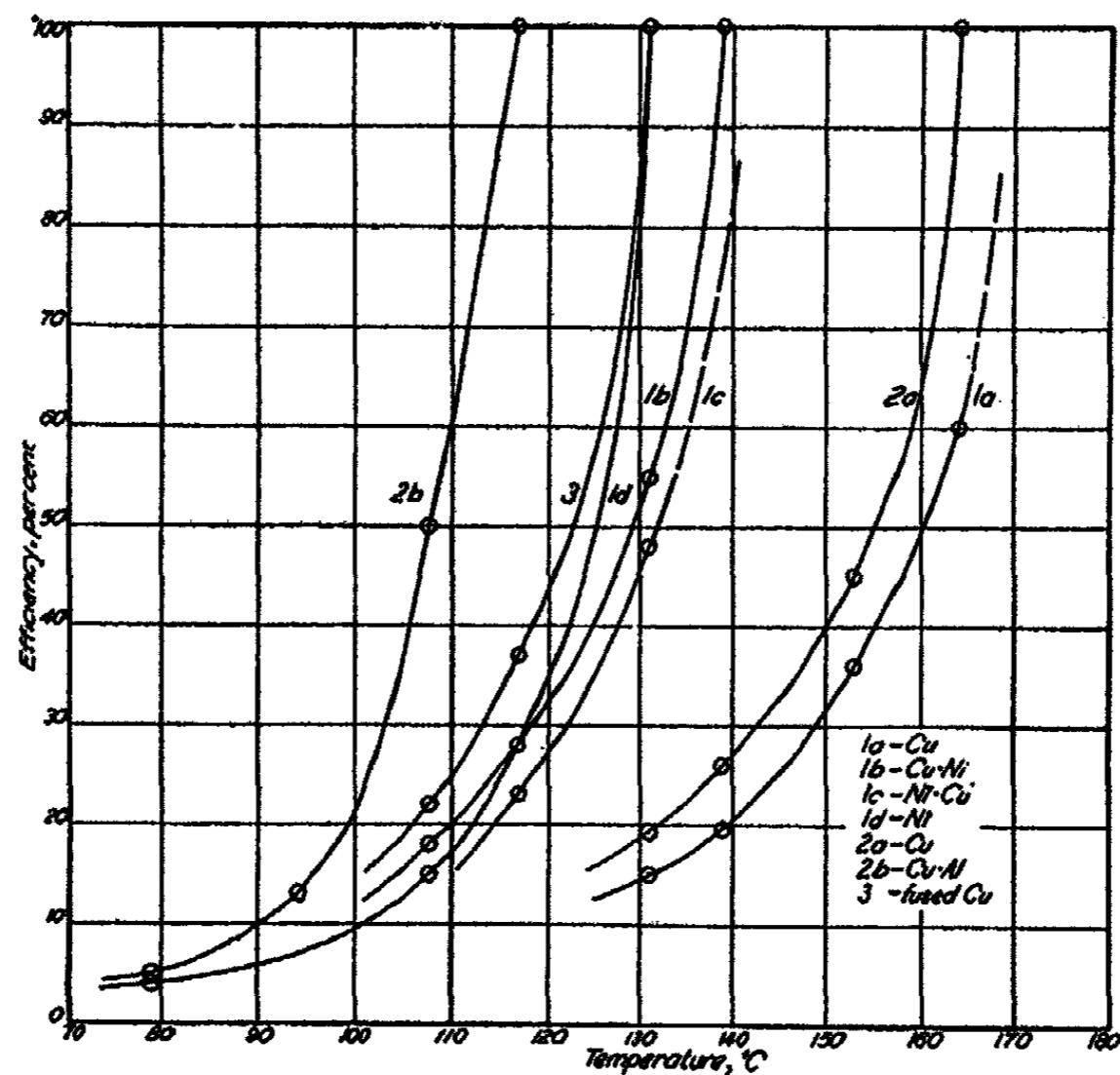


FIG. 3
Temperature-efficiency curves for the steady state synthesis

sense 100 per cent. efficient. If leakage begins, however, the catalyst is clearly not converting all available oxygen to water, and to the extent that it fails to do this, its efficiency is less than 100 per cent. It is correct, therefore, to calculate catalytic efficiencies on the basis of the oxygen entering the catalyst chamber only when there is complete conversion of this oxygen to water, or when there is leakage of oxygen gas thru the catalyst bed.

In a study of the mechanism of a catalytic reaction, it is the steady state conditions which are of most importance. The curves in Fig. 3 show the change in efficiency with temperature for the catalysts in this final steady state. The points plotted are taken from the results of "continuous" runs lasting many days, during which time the temperature of the catalyst was varied back and forth several times over the range indicated. As already

mentioned, continued use of the catalysts resulted in a decreased volume, and this was in general accompanied by a decrease in the catalytic efficiency and the amount of oxide formed in a given time. Successive runs, however, gave closely reproducible results, and the deterioration of the catalysts tended to approach a limiting value, both as regards efficiency and oxide formation. The points shown in Fig. 3 were obtained late in the series of runs with any one catalyst, and represent therefore the efficiencies of the catalysts near this limiting state.

Those points plotted as 100 per cent. efficiency are, in a way, fortuitous. The catalyst in its oxidized condition was heated to successively higher temperatures until the oxide "broke," i.e., reduction of the stable oxide took place. Since heating was effected by means of vapor baths, there was necessarily a discontinuity in going from one temperature to another. In the cases of catalysts Nos. 1a and 1c, reduction of the oxide started immediately and rapidly at the higher temperature. With the other catalysts, reduction progressed much more slowly and in some cases did not start until some time after the higher temperature was reached. The results obtained with fused copper, N. 3, may be given as an example. At 117° the efficiency was 37 per cent. When the temperature was raised to 131°, the efficiency increased immediately to 82 per cent. During the next 14 hours, there was a slow increase in efficiency to 99 per cent. and visible reduction of the oxide started at the top of the catalyst bed where the concentration of free oxygen was least. During the next 24 hours, the efficiency was 100 per cent., the oxygen leakage remained nil, and reduction progressed very slowly downwards for a distance of one-half centimeter. At no time was the rate of water formation greater than 10 mg. per 5 min., and since there was no leakage of free oxygen, reduction must have taken place at a rate too small for measurement. On lowering the temperature to 117°, the reduced portion of the catalyst was again oxidized. It is believed, therefore, that 131° is, within a small limit of error, the minimum temperature at which the stable oxide formed on this catalyst is reduced under the conditions of the steady state synthesis. In other words, it is the lowest temperature at which the catalyst is 100 per cent. efficient.

Similar points were obtained for catalysts Nos. 1b, 1d, 2a, and 2b, altho in none of these cases was reduction as gradual as in the example just given. It is possible, and perhaps probable, that the minimum temperatures of reduction for these catalysts are slightly lower than the points obtained, but these latter can not be greatly in error since the extrapolated curves pass smoothly thru them.

The catalysts in order of decreasing efficiencies in the final steady state are copper-alumina, fused copper, nickel, nickel-copper, copper-nickel, and pure precipitated copper. There is no mixture effect in the copper-nickel series, each constituent seeming to act independently of the other. At the lower temperatures, the nickel-copper is more active than is pure nickel, but in all other cases there is a gradual change in efficiency from nickel to copper. It is of interest to note that the amounts of shrinkage in the preliminary treat-

ment and reduction parallel exactly the efficiencies in the final steady state. Precipitated copper, which shrank most of all, is by far the poorest catalyst, while copper-alumina, fused copper, and nickel, which shrank least, are the best catalysts. Of the two precipitated coppers, that having the harder original granule, No. 2a, shrank less and was somewhat more active catalytically.

A comparison of total amounts of oxide formed by the catalysts and their efficiencies shows another parallel relation. The catalysts which are most active catalytically are also those which possess the greatest capacity for forming oxide. The amount of oxide formed by a given catalyst in the final steady state increases slowly with the length of time it is run without reduction, and there is an accompanying slow decrease in the efficiency of conversion. On the other hand, a freshly reduced catalyst forms during a given time more oxide and is more efficient than a catalyst which has been used for some time. This difference is most marked in the case of the poorer catalysts, and is but slightly evident in the case of a catalyst such as copper-alumina. Undoubtedly this behavior is related to the gradual shrinkage of the catalyst in use and the accompanying change in the physical nature of the surface. That the amount of oxide present is not directly related to the catalytic efficiency is shown clearly by the following data. Catalyst 2b, copper-alumina, was 90 per cent. efficient with 92.2 mg. water-equivalent of oxide present, and in a subsequent run at the same temperature gave a conversion of 84 per cent. with only 42.6 mg. water-equivalent of oxide on its surface. Catalyst 1b, copper-nickel, gave at different times identical conversions of 29 per cent. with 48.2 mg. and 25.0 mg. water-equivalent of oxide present respectively. It can be said in general that a catalyst which is active catalytically is also active in forming oxide, but there is no evidence that the former is a result of the latter.

Because of the tendency to continue the formation of oxide for long periods of time, it was difficult to obtain quantitative data on the relative "saturation" values for oxide formation by the different catalysts. The data are further complicated by the differences in temperatures at which the catalysts were run, and the resulting changes in their rates of oxide formation. The following figures, obtained from runs lasting many hours, are given, therefore, not as absolute, but with the idea of showing relative values for the different catalysts. The figures represent water-equivalents of oxide expressed as milligrams of water per gram of reduced catalyst: copper-alumina, 100; copper-nickel, 30; nickel-copper 27; nickel, 13; fused copper, 12; precipitated copper, No. 2a, 4; and precipitated copper, No. 1a, 2.5. Due to the great difference in density of the precipitated catalysts as compared with the fused copper, a comparison of relative oxide formation based on unit weights has little significance in the latter case. A better comparison is that of total amounts of oxide formed by the three catalysts: copper-alumina, fused copper, and copper-nickel. The volumes of these catalysts were each about 2 cc., and the amounts of oxide were 197 mg. water-equivalent for the copper-alumina, 74 mg. for the fused copper, and 48 mg. for the copper-nickel. The catalysts in

order of decreasing capacities for forming oxide are, therefore, copper-alumina, fused copper, copper-nickel, nickel-copper, nickel, and precipitated copper.

It is evident that there is here a distinct mixture effect in the copper-nickel series. The addition of either metal to the other increases markedly the capacity for forming oxide during the catalytic synthesis of water. Moreover, the copper forms less oxide than does nickel, the mixture containing 88 per cent. copper forms more oxide than the one containing 75 per cent. nickel. This is the only instance of a mixture effect found in this series. That there is not a corresponding effect in the catalytic efficiencies indicates that there is no direct relation between oxide formation and the catalytic mechanism.

The changes in efficiency and oxide forming capacity caused by heating the catalysts to 444° are of interest in connection with changes in the physical structure of the catalysts which took place at this temperature. In all cases there was appreciable shrinkage of the catalysts, a decreased oxide forming capacity, and with but one exception, which was in the case of nickel, an accompanying decrease in catalytic efficiency. The catalyst least affected by the heat treatment was copper-alumina, which shrank only slightly, with no apparent sintering of the separate granules. The efficiency, as determined by six-hour runs immediately before and after the heat treatment, was practically unchanged, but the total amounts of oxide formed during this length of time were 42.6 and 35.6 mg. water-equivalent respectively. The fused copper catalyst shrank about one-eighth and some sintering was evident. The change in efficiency was very great: before heating, a six-hour run gave a maximum of 9.4 mg. water per 5 min. decreasing to 7.5 mg. at the end of the run; after heating, the maximum was 2.4 mg. per 5 min. and the final rate only 1.3 mg. The oxide formed in this time was 13.0 mg. water-equivalent before and 7.4 mg. after the treatment. Precipitated copper shrank to about half its previous volume, and the granules sintered together, holding the shape of the catalyst tube so that considerable jarring was necessary to separate them. Both efficiency and oxide formation decreased more than half. The copper-nickel mixtures suffered a large decrease in both efficiency and oxide forming capacity.

The nickel catalyst shrank nearly 50 per cent. and sintering took place in a manner similar to that described for the precipitated copper. The oxide formation in six-hour runs decreased from 17.2 mg. water-equivalent before heating to 5.0 mg. after; but the catalytic efficiency *increased* from a maximum of 9.4 mg. water per 5 min. lasting 2 hours and a final value of 0.8 mg., to a maximum of 9.8 mg. per 5 min. lasting the full six hour period. Subsequent runs showed a gradual decrease in efficiency and oxide formation, but the efficiency did not, in the entire period of 20 days during which the runs were continued, reach the low value obtained before the heat treatment. Successive runs gave maximum rates of (1) 9.8 mg. water per 5 min. for nearly 6 hours, decreasing to 3.7 mg. at the end of the next hour, and forming 4.2 mg. water-equivalent of oxide; (2) 9.8 mg. per 5 min. lasting 2 hours and falling to 2.1 mg. in six hours, with oxide equivalent to 3.0 mg. water; and (3) 9.8 mg.

water for 1 hour, falling to 1.6 mg. in 6 hours, and forming 3.0 mg. oxide. There is apparent a gradual change toward the previous condition of the catalyst as regards catalytic efficiency but not as regards oxide-forming capacity.

Discussion

The essential likeness of the two apparently different types of initial reaction has been pointed out in the last section. Whether there will be a continued maximum with no oxygen leakage, or a short maximum with leakage starting almost immediately, is apparently dependent on the rates of the two competing reactions which are in evidence during the initial stage of catalysis. If the temperature is sufficiently high, the rate of synthesis will rise to give complete conversion, and there is no reason to expect a decrease in this rate unless the catalyst deteriorates due to a physical change.

At a somewhat lower temperature, where the conversion is not quite complete and the remaining fraction of the oxygen is completely taken up by the metal to form oxide, the duration of the continued maximum will depend on the magnitude of this fraction and on the capacity of the metal for forming oxide. As the temperature is lowered, the duration will decrease owing to the decreased rate of synthesis and the resulting increase in the amount of oxygen available for forming oxide, but there will be a continued maximum as long as the rate of oxide formation and the capacity of the metal are sufficiently great to prevent the escape of free oxygen past the catalyst. When this latter occurs, however, the catalyst surface has become covered with a layer of oxide, and the rate of synthesis will undergo an immediate decrease. On the other hand, when the rates of synthesis and oxide formation are both low, the oxygen leakage starts immediately and a short maximum results. It is evident from the experimental data that the expected transition from the continued maximum at high temperatures to the short maximum at low temperatures takes place at fairly high temperature in the case of copper, but has not been completely attained at 34° in the case of nickel.

Evidence that the formation of oxide and the catalytic process are independent and competing reactions is to be found in the observed increase in the rate of the latter during the initial stage. The catalyst is, as already shown, 100 per cent. efficient during this period when the formation of oxide is progressing thru the catalyst mass; and the formation of water takes place chiefly at, or just beyond, the oxide-metal boundary where the heat effect is greatest. Nevertheless, the oxide covered portion of the catalyst is active to some extent in the synthesis, and since the formation of further oxide on such surface is extremely slow, the amount of water formed on this surface must gradually increase as its length and area increase. With a sufficiently long column of catalyst a limiting state will be reached in which all the oxygen is converted to water on the oxide covered surface, and no free oxygen will be left to extend it farther. This has actually been observed in the case of copper whose oxide is visible. In the case of an insufficient depth of catalyst, however, the oxidation will progress until the whole surface is covered, and at

this point there will be a drop in the rate of water formation except in the marginal case in which the depth of catalyst is just sufficient to effect complete conversion on the oxide covered surface.

The suppression of the oxidation reaction on the oxidized portion of the catalyst thus causes an increase in the rate of synthesis in the first stage and this may reach the point where complete conversion is attained. On the other hand, the covering of the entire catalyst by oxide results in a marked decrease in the rate of synthesis, since such a surface is less active than is one of free metal. In other words, the oxide layer acts as a poison by covering the more active metal surface.

Further evidence for the independence of the catalytic mechanism and the formation of oxide is given by the absence of any mixture effect in the former and its presence in the latter. It seems highly probable that, if the catalytic mechanism involved the stable oxide, an effect which clearly influences the formation of the latter would have a corresponding influence on the catalytic efficiency.

In the final steady state, the formation of further oxide takes place at an extremely slow rate, and this reaction is, therefore, no longer in serious competition with that of catalysis. Since reduction of the stable oxide is inhibited by free oxygen, which is always present when conversion is not complete, it does not seem probable that this oxide is an important factor in the catalytic mechanism. There is another and faster reaction most in evidence during the initial stage, and this undoubtedly continues to play a predominant part in the true catalytic mechanism of the steady state.

The catalyst surface is probably at no time *completely* covered by oxide; copper (or nickel) nuclei are no doubt present at isolated portions of the oxide layer, and it is these nuclei which effect most of the catalytic synthesis. The probable mechanism of the catalysis seems to be activation of an oxygen molecule or atom by its close approach to an active metal atom with the probable formation of an "indefinite" oxide which is readily attacked by hydrogen. It is possible that the hydrogen is activated in a similar way, but the present data do not show whether this is probable or not. Whether an oxide-metal interface is necessary to the synthesis is not definitely shown, but it seems likely that this is not the case. The approach of a single oxygen molecule to an active atom on a free metal surface seems all that is necessary for its activation. At the beginning of the initial stage the whole surface is probably catalytically active, and it is the formation of the stable oxide which decreases this active surface and finally causes the decrease in efficiency.

The relation between hardness of granule, shrinkage, the effect of heating, capacity for forming oxide, and catalytic activity give important information for explaining the catalytic reaction. The experimental results show that those catalysts which undergo greatest shrinkage in the preliminary treatment and reduction are also lowest in catalytic efficiency and oxide forming capacity. Of the two precipitated copper catalysts, the more active was the one having the harder original granule and undergoing the lesser amount of shrinkage. In the series of copper catalysts, the efficiencies paralleled closely

the effects mentioned above. The most efficient of these catalysts was the copper-alumina and this was also most active in forming oxide, suffered least shrinkage, and was least affected by the heat treatment. The fused copper underwent but slight shrinkage and formed large amounts of oxide, but it suffered great injury on heating. The poorest catalysts, the precipitated coppers, shrank largely, formed but little oxide, and were further greatly inactivated by heating.

The behavior of copper-alumina is especially interesting when compared with promoted ammonia catalysts. It has been shown¹ that the promoters used in ammonia catalysts (usually aluminum and potassium oxides) serve to keep the surface of the reduced catalyst relatively large. The function of alumina in the copper-alumina seems to be similar in that it prevents the collapse of the catalyst structure.

These facts are in agreement with the theory of the catalytic surface developed by Professor H. S. Taylor² in several articles. On the basis of this theory, a catalyst like copper-alumina should be very active. Owing to the presence of the aluminum oxide as a supporting network, shrinkage during the preliminary treatment and reduction should be slight, and there should be on the reduced catalyst a relatively large number of copper atoms in an unsaturated condition. For the same reason rearrangement of the copper atoms should be relatively slow, and even high temperature should have no great effect. Pure precipitated copper should, on the other hand, be much more affected in these ways. Reduction should cause shrinkage, and the ready mobility of the unsupported copper atoms should leave a surface with but few exposed edges and corners. The fused copper catalyst shrank only slightly in the preliminary treatment and reduction, but heating to 444° caused a greater change. It seems probable that the oxide remaining in the interior of the granule acted as a support to the atoms of metal on the surface, and that the removal of this oxide resulted in a collapse of the catalyst structure.

A catalyst having active atoms in the sense pictured by the theory should show a parallel relation in the amount of oxide formed and its catalytic activity, and this is borne out by the experimental facts. A similar relationship has been shown for ammonia catalysts by Almquist and Black.³ They find that those catalysts which are most active in the ammonia synthesis are also the ones which form the largest amounts of oxide when exposed to nitrogen-hydrogen mixtures containing small amounts of oxygen or water vapor.

Nickel shrank but little in the preliminary treatment and reduction, and it was much more active than precipitated copper. The original granule was firmer and the mobility of the nickel atom is less than that of copper,—all of which agrees with the theory. The result of heating nickel to 444° is, however, entirely different from that to be expected. There was a decrease in oxide forming capacity in agreement with previous results with other catalysts,

¹ Wyckoff and Crittenden: *J. Am. Chem. Soc.*, 47, 2866 (1925).

² Taylor: *Proc. Roy. Soc.*, 108A, 105 (1925); Fourth Report of the Committee on Contact Catalysis, *loc. cit.*; and others.

³ Almquist and Black: *J. Am. Chem. Soc.*, 48, 2814 (1926).

but in spite of a large amount of shrinkage and the sintering of the separate granules, the catalytic activity was considerably increased. The present data do not warrant any definite explanation of this phenomenon, but it is extremely interesting to note that nickel behaves abnormally in respect to many of its physical properties when heated above about 360°. There is a change in magnetic properties, in the coefficient of expansion, and in the cooling curve of nickel at this transition temperature. These effects are not permanent, and this is in agreement with the observed tendency of the catalyst to return to its former lower activity.

Benton and Emmett¹ try to show that the stable oxide is an essential step in the catalytic mechanism with nickel. Their results, however, show that if the oxygen is shut off during the final steady state, the rate of reduction of this oxide with pure hydrogen is very much less than the rate of water formation during the synthesis immediately preceding. Since reduction of the oxide is inhibited by the free oxygen present during the synthesis, the rate of water formation should, if the synthesis involves reduction of this oxide, be *increased* by shutting off the oxygen. This was never the case with the catalysts used by Benton and Emmett. Even if the oxygen is shut off during the initial stage, before the oxide has spread entirely over the catalysts surface, the rate of induction is in no way comparable with the rate of synthesis. These authors admit that "unless the rate of reduction *in the catalytic process* is much greater than the rates here observed, successive oxidation and reduction can have only a minor share in the catalytic mechanism." The rates of reduction referred to are for a partially oxidized surface, having therefore a large oxide-metal interface, and are with pure oxygen-free hydrogen. In the steady state, the catalyst surface is covered with oxide, thus giving a much smaller interface between oxide and metal, and appreciable amounts of free oxygen are present. Since reduction of nickel oxide takes place at the interface and is inhibited by free oxygen, it does not seem possible that its rate can be greater under such adverse steady state conditions.

These authors say further, "there is no reason to suppose that the interfacial area between the oxide and the nickel was of the same order of magnitude in the reduction as in the catalytic experiments," and "an 8- or 10-fold increase is all that is necessary to make the observed reduction rates equal to the rates of catalysis." But here they fail to distinguish between the initial stage and the true catalysis of the final steady state. It is hardly conceivable that shutting off the oxygen in the final steady state can *decrease* by 8- or 10-fold the interfacial area, an assumption necessary to explain the observed facts on the basis of their theory. On the contrary, the interface should at first increase in area, since oxygen gas is no longer present to "heal" the break in the oxide film. Therefore, if reduction of the stable oxide accounts for most of the water formed during catalysis, there should be *in all cases* (provided, of course, sufficient oxide is present) a considerable increase in the rate of water formation at the instant of shutting off the oxygen. This is contrary to the observed facts.

¹ Benton and Emmett: J. Am. Chem. Soc., 48, 632 (1926).

In referring to the interpretation given in our first paper, Benton and Emmett state that it was "not realized (by Larson and Smith) that the reduction of nickel oxide by hydrogen is an autocatalytic process." This is incorrect. Whether or not the reduction is autocatalytic is of little importance unless reduction is free to take place. That it is not free to do this in the presence of gaseous oxygen at the temperatures in question is well established, and it was this consideration that led to our conclusion that the stable oxide "probably contributes little to the total water being formed."

It was found in our earlier work, however, that under certain conditions, shutting off the oxygen in the final steady state caused a considerable and immediate increase in the rate of water formation. Were it not for the known inhibiting action of free oxygen on the reduction, and the evidence of a much faster reaction in the initial and later stages, this would support the theory involving the stable oxide. In view, however, of these factors, as well as of the fact that there is not *in all cases* such an increase, this mechanism does not appear to be a probable one, and the theory presented in the first paper seems to require no modification.

It is necessary to recognize, however, that the most probable mechanism as postulated in that and the present paper, may differ from that of alternate oxidation and reduction merely in degree. The distinction is analogous to that between an isolated molecule or atom of oxygen adsorbed on a clean metal surface, and an extended film of metallic oxide. It is commonly recognized in the latter example that there is no sharp dividing line between the two. It seems important, nevertheless, to distinguish between the stable oxide and a molecule of oxygen which becomes activated by its close approach to an active metal atom. It is no doubt due to its capacity for forming oxide that the catalyst is able to activate an oxygen molecule and render it capable of ready union with hydrogen.

The most probable mechanism for the water synthesis over copper and nickel catalysts appears, then, to be activation of oxygen molecules or atoms with the resulting formation of an "indefinite" oxide, by which they are opened to attack by hydrogen. It seems reasonably certain that the synthesis in the steady state is much more rapid than can be accounted for by reduction of the stable oxide, and for this reason the mechanism postulated by Benton and Emmett appears to play but little part in the true catalytic reaction.

The author wishes to thank Professor William C. Bray for his interest in this problem and the many valuable suggestions he has made, both during the experimental part and in the writing of this paper.

Summary

The following catalysts have been studied in the water synthesis reaction at temperatures between 75° and 180° , and with an oxygen concentration of 2.4 per cent.: copper, nickel, two mixtures of these metals, a mixture of copper and alumina,—all prepared by reduction of the precipitated hydroxides; and a sample of copper prepared by reducing the fused oxide.

The most efficient catalysts in the final steady state synthesis were also those which formed the greatest amounts of oxide during the catalysis, and which underwent least change in physical structure on reduction and later heat treatment. The catalysts in order of decreasing catalytic efficiencies are copper-alumina, copper from fused oxide, nickel, nickel-copper, copper-nickel, and copper from the precipitated hydroxide.

No mixture effect was found in the copper nickel series as regards catalytic efficiency, but one was clearly evident with respect to the amount of oxide formed during catalysis.

Heating the catalysts to 444° for one-half hour caused a decreased efficiency except in the case of nickel. It is suggested that the anomalous behavior of the latter may be related to the existence of a transition point at about 360° which causes changes in the physical properties of the metal.

The importance of the physical nature of the catalyst surface has been emphasized. The experimental results are in agreement with the theory of the catalyst surface developed by Professor H. S. Taylor.

The probable mechanism of the catalysis appears to be interaction of hydrogen molecules and activated oxygen molecules or atoms, probably in the form of an "indefinite" oxide, at points of greatest activity on the catalyst surface. It has been shown that the stable oxide probably plays but little part in the synthesis and that, therefore, the theory postulated by Benton and Emmett involving this oxide, is not supported by the experimental facts. The formation of the stable oxide seems to be an unavoidable side reaction which ultimately results in partial poisoning of the catalyst.

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THE APPLICATION OF THE THIRD LAW OF THERMODYNAMICS TO SOME ORGANIC REACTIONS

BY GEORGE S. PARKS AND KENNETH K. KELLEY

Preliminary Discussion

Probably the most satisfactory statement of the proposed third law of thermodynamics is that of Lewis and Gibson¹: "If the entropy of each element in some crystalline form be taken as zero at the absolute zero, the entropy of any pure crystal at the absolute zero is zero, and the entropy of any other substance is greater than zero." The last portion of this statement was prompted partly by theoretical considerations and partly by evidence adduced from the data of Gibson, Parks and Latimer² on the specific heats of ethyl and n-propyl alcohols and their equimolar mixture. From these data it appeared that at 0°K. the entropy of a solution probably exceeds that of the pure components by a small finite value and the entropy of glassy ethyl alcohol may possibly exceed that of the crystals by about 1.08 units per mol. More recently this comparison between the glassy and liquid states has been made in a more convincing fashion in the case of glycerol. In studies upon this substance by Simon³, by Gibson and Giaouque⁴, and finally by Simon and Lange⁵ the heat capacity measurements have been carried down to 10.6°K. with the result that the estimated entropy of the glass at 0°K. exceeds that of the crystals by 4.6 (± 0.3) units per mol. New data on the heat capacities of the glass and crystals in the cases of both ethyl⁶ and n-propyl⁷ alcohol point to the same conclusion: namely, that the entropy of a glass at the absolute zero exceeds that of the corresponding crystalline form.

Considerations such as these have led Eastman⁸ to suggest that a pure crystalline substance has a positive, tho probably small, value for its entropy at the absolute zero, if the unit of structure of the crystal contains a large number of atoms. In this respect such a compound would bear a general resemblance to a glass and would differ from it merely in degree. Such compounds with complex cell units and finite positive entropies at 0°K. would probably be found largely in the field of organic chemistry. However, more recently Pauling and Tolman⁹, applying the methods of statistical mechanics, have deduced the conclusion that "the entropy of a perfect crystal

¹ Lewis and Gibson: *J. Am. Chem. Soc.*, **42**, 1533 (1920).

² Gibson, Parks and Latimer: *J. Am. Chem. Soc.*, **42**, 1542 (1920).

³ Simon: *Ann. Physik*, (4) **68**, 260 (1922).

⁴ Gibson and Giaouque: *J. Am. Chem. Soc.*, **45**, 93 (1923).

⁵ Simon and Lange: *Z. Physik*, **38**, 227 (1926).

⁶ Parks: *J. Am. Chem. Soc.*, **47**, 341 (1925).

⁷ Parks and Huffman: *J. Am. Chem. Soc.*, **48**, 2791 (1926).

⁸ Eastman: *J. Am. Chem. Soc.*, **46**, 43 (1924).

⁹ Pauling and Tolman: *J. Am. Chem. Soc.*, **47**, 2156 (1925).

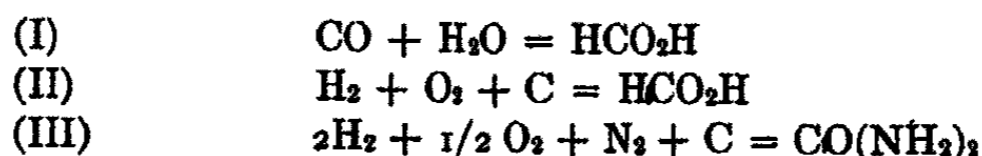
at the absolute zero is not dependent on the complexity of the unit of crystal structure", in distinct contradiction to this suggestion by Eastman.

From a practical standpoint the first portion of the preceding statement of the third law of thermodynamics, that providing for zero entropy for a pure crystalline substance at the absolute zero, is of such importance to physical chemistry that it should be thoroly tested experimentally. This may be done in the case of a given reaction at a definite temperature by comparing the entropy change, ΔS , calculated from heat capacity data on the assumption of the third law with the corresponding value for ΔS calculated indirectly from the free energy change (ΔF) and the change in heat content (ΔH) by means of the fundamental relationship,

$$\Delta F = \Delta H - T\Delta S. \quad (1)$$

Such a comparison, in order that it may have any real significance, requires very accurate data; since several types of experimentally measurable quantities are involved and even moderate errors in these, if cumulative, may produce astonishing discrepancies. For inorganic reactions involving pure crystalline substances a considerable number of these tests have been made and in general it has been found that the more reliable the data obtainable the better is the agreement with the requirements of the third law. Thus, for instance, Lewis and Gibson¹ in 1917, reviewing the data for nine such tests, found an average discrepancy of 1.6 entropy units; while a few years later Lewis, Gibson and Latimer², using the extremely accurate electromotive force measurements of Gerke, found in the case of three of these reactions involving chlorides that the average apparent deviation from the third law had been reduced tenfold. Hence, insofar as simple, crystalline, inorganic compounds are concerned, the third law as stated at the beginning of this paper seems to have been placed on a very firm basis.

In the field of organic chemistry the situation is quite different. Organic compounds in general do not lend themselves to simple, reversible reactions involving the elements and suitable for the measurement of equilibria. Still fewer of them are involved in such reactions as may be studied by electromotive force measurements with a reversible galvanic cell. Hence, the third law of thermodynamics, if valid, serves as a very valuable tool for the calculation of the free energies of organic substances by the sole use of thermal data, such as heats of combustion and low temperature heat capacity values. We say "if valid" because it is precisely in the field of organic compounds that the tests of the third law have been fewest and least satisfactory. In 1923, when the present investigation was undertaken, the only earlier work on this question was that of Gibson, Latimer and Parks³ dealing with the following three reactions:



¹ Lewis and Gibson: *J. Am. Chem. Soc.*, 39, 2580 (1917).

² Lewis, Gibson and Latimer: *J. Am. Chem. Soc.*, 44, 1014 (1922).

³ Gibson, Latimer and Parks: *J. Am. Chem. Soc.*, 42, 1533 (1920).

For the purposes of the moment we have now revised and corrected their data in the light of the later information given by Lewis and Randall¹. The final results are summarized in Table I. In the case of the first two reactions the values for ΔF_{298}° calculated by Lewis and Randall have been corrected by means of vapor pressure data recently obtained for formic acid by Ramsperger and Porter². The ΔS_{298} values found by Equation 1 appear in the fourth column of the table. The corresponding values (Column 5) calculated on the assumption of the third law have been obtained by use of the latest table for the entropies of the elements.³ In all cases we have attempted to estimate the maximum errors in these ΔS figures.

TABLE I
Summarized Data for Earlier Tests of the Third Law

| Reaction | ΔF_{298}° cal. | ΔH_{298} cal. | ΔS_{298} , cal./degree | |
|----------|----------------------------------|--------------------------|--------------------------------|---------------------|
| | | | by equation 1 | by third law |
| I | + 4,100 | - 5,200 | - 31.2 (± 6) | - 28.4 (± 4) |
| II | - 85,000 | - 99,700 | - 49.3 (± 7) | - 44.5 (± 4) |
| III | - 47,280 | - 78,800 | - 105.7 (± 8) | - 88.7 (± 10) |

A comparison of the ΔS results obtained by the two different methods shows that in the case of all three reactions the agreement is within the limits of maximum error in the quantities involved. However, these possible errors are very large and from the data just given we are only justified in concluding that the third law is roughly valid for organic reactions. This situation, in view of the increasing tendency to assume the exact validity of the third law in the case of organic reactions, calls for further and, if possible, more accurate tests. The present study has been undertaken to partially fill the need.

Perhaps, before proceeding further, it will be well to analyze the problem so that we may see wherein the uncertainties in the ΔS values are apt to arise. ΔS calculated by Equation 1 obviously depends upon the accuracy of the values for ΔF and ΔH . Now ΔF in these tests is ordinarily the result of equilibria measurements and in some cases can be determined with a fairly high degree of accuracy, especially if only one reaction is involved and the temperatures concerned are close to that of the room. If on the other hand, as in reactions II and III, the value for ΔF is the result obtained by the addition of several equations and their corresponding ΔF quantities, the errors may be cumulative and the uncertainty in the final value will mount with surprising rapidity. Thus, in reaction II a possible error of 210 calories in the free energy of formation of CO^4 alone contributes thereby an uncertainty of 0.7 entropy unit in the final result. Equally important are errors in the ΔH values. In some reactions the change in heat content, ΔH , may

¹ Lewis and Randall: "Thermodynamics," pp. 578, 585 (1923). Here and thruout the remainder of this paper we shall employ their notation and methods.

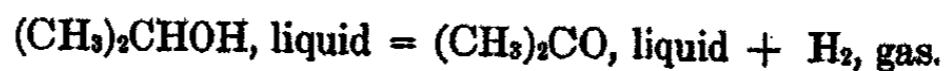
² Ramsperger and Porter: J. Am. Chem. Soc., 48, 1272 (1926).

³ Lewis, Gibson and Latimer: J. Am. Chem. Soc., 44, 1016 (1922).

⁴ Eastman and Evans: J. Am. Chem. Soc., 46, 902 (1924).

be obtained directly by a calorimetric method or indirectly from measurements of the e.m.f. of a galvanic cell or of equilibria over a range of temperatures. These indirect methods are frequently of greater accuracy than the calorimetric. Especially is this likely to be true in the case of organic reactions in which heats of combustion are used, because most of the combustion data now available is from early work and may involve errors of one per cent or more. Thus, in the case of reactions I and II an error of 600 calories (1%) in the heat of combustion of formic acid produces an equal error in the ΔH values and an error of 2.0 units in the entropy change in Column 4. On the other hand, considering the ΔS values calculated by the third law, we find that they are probably good to about one or two per cent when entirely dependent on accurate specific heat data. However, in cases such as the entropies of formic acid and urea the experimental data did not go below liquid air temperatures and it was necessary to use the "n formula" of Lewis and Gibson¹ for extrapolation to 0°K. This relationship when applied to organic compounds constitutes, we believe, only a first approximation and may involve errors of even 25% in estimating the entropies below 90°K. Thus, for instance, we estimate that the entropy of formic acid, obtained by this formula, may possibly be in error by 3.0 units.

In view of all these considerations, the reaction which we in 1923 selected for again testing the third law was the following:



Sabatier² had shown that this reaction in the gaseous phase was reversible and later Rideal³ had measured the equilibria involved over a range of temperatures by means of a static method. His results, however, were rather uncertain, owing to the great possibility of side reactions with such a procedure. We in the present study have employed a dynamic method and have obtained the equilibrium constant at several temperatures. From this series of equilibrium constants we have finally obtained ΔF_{298}° and ΔH_{298}° for the above reaction. We have also measured the heat capacities of iso-propyl alcohol and acetone from 70° up to 298°K. and in this way we have been able to calculate the corresponding entropies at 298° on the assumption of the third law. Of course, in estimating the entropy increases for these compounds from 0° to 70°K. we have been forced to employ some extrapolation method and so have had recourse to the afore-mentioned formula of Lewis and Gibson. However, as we are later concerned with the difference between the entropies of these two compounds in obtaining ΔS_{298}° , any error arising from use of the "n formula" is minimized in this case and is probably not greater than 1.0 entropy unit. The entropy of a mol of hydrogen at 298°K. is also involved but this is probably known with considerable accuracy; in fact, Lewis, Gibson and Latimer consider their figure to be good to better

¹ Lewis and Gibson: *J. Am. Chem. Soc.*, 39, 2565 (1917).

² Sabatier (Reid): "Catalysis in Organic Chemistry," p. 236 (1922).

³ Rideal: *Proc. Roy Soc.*, 99A, 153 (1921).

than one-tenth of a unit. All in all, then, this organic reaction serves as a very promising test of the third law¹.

Within the last few years sufficient data have accumulated in the literature to provide for another very good test in the case of the reaction:



This chemical change is very similar in principle to the preceding one. Therefore, we shall briefly consider it after first presenting our data for the iso-propyl alcohol, acetone reaction.

Experimental

The experimental work owing to the nature of the problem resolved itself into two distinct parts, which here will be considered separately.

Materials. During the course of the investigation several samples of iso-propyl alcohol were prepared and used. In our purification process "refined" iso-propyl alcohol was first dehydrated by two successive distillations over lime in the ordinary manner. In each instance the resulting product was carefully fractionated and the middle portion, about 60% of the total, was selected for the measurements. The average density of these middle portions was 0.78093 at 25°/4°, which corresponds to 99.96% alcohol on the basis of the criteria² previously employed.

Pure, absolute acetone, obtained from the National Aniline and Chemical Company, was used without further purification for the heat capacity determinations of Part I. For the equilibrium measurements of Part II the ordinary C.P. acetone of commerce was purified by treatment with anhydrous calcium chloride as in the work of Parks and Chaffee.³ After the final fractionation process, the middle portion representing about one-half of the total was selected for use. It distilled between 56.1° and 56.2°C. and had a density of 0.7855 at 25°/4°.

Part I: Heat Capacity Data

In principle, the method of Nernst was employed with an aneroid calorimeter in determining the "true" specific heats and the fusion data. A measured amount of heat was supplied by an electric current to the substance

¹ In connection with this test of the third law there is one point which should be noted. If the entropy of hydrogen at 0° K be taken as zero, then according to Eastman's argument it is conceivable that the two compounds in question, iso-propyl alcohol and acetone, may have small positive entropies, possibly of the order of two or three tenths of a unit, at the absolute zero. Furthermore, if this be true, these values will more or less cancel one another in the subsequent calculation of ΔS_{298} and the result will not differ appreciably from that obtainable on the basis of zero entropies at 0° K. Hence, our present test cannot be used to either prove or disprove Eastman's speculations, as the possible experimental error in our ΔS_{298} value obtained from the heat capacity data is at least 1.0 entropy unit or, perhaps, five times the magnitude of any such hypothetical effect. However, Eastman's argument is really of theoretical rather than of practical interest insofar as the simpler organic compounds are concerned, and in the present paper we are primarily involved with the question of the applicability of the third law as a fairly accurate, useful tool for the calculation of free energies. Certainly for such a practical purpose the above reaction serves very well for testing the (at least approximate) validity of the third law in the field of organic chemistry.

² Parks and Kelley: *J. Phys. Chem.*, 29, 728 (1925).

³ Parks and Chaffee: *J. Phys. Chem.*, 31, 440 (1927).

contained in a copper calorimeter, which was suspended in a vacuum and surrounded by a silvered copper cylinder in order to diminish the conduction and radiation of heat to and from the surroundings. A thermocouple in the center of the calorimeter measured the rise in temperature. The entire apparatus and details of experimental procedure have been fully described in other places.¹ In view of the accuracy of the various measurements involved,

TABLE II
Specific Heat Values for Iso-Propyl Alcohol

| Crystals | | Liquid | |
|-----------|-------------|-----------|-------------|
| Temp., °K | Cp per gram | Temp., °K | Cp per gram |
| 70.7 | 0.172 | 195.4 | 0.443 |
| 76.6 | 0.182 | 198.5 | 0.446 |
| 82.7 | 0.192 | 199.1 | 0.447 |
| 88.5 | 0.201 | 227.0 | 0.472 |
| 88.9 | 0.201 | 275.3 | 0.553 |
| 92.2 | 0.208 | 275.6 | 0.554 |
| 92.7 | 0.207 | 284.0 | 0.576 |
| 93.0 | 0.208 | 287.6 | 0.582 |
| 95.2 | 0.212 | 290.2 | 0.592 |
| 95.9 | 0.212 | 290.3 | 0.590 |
| 99.7 | 0.219 | 293.1 | 0.601 |
| 100.9 | 0.221 | | |
| 101.3 | 0.220 | | |
| 106.5 | 0.227 | | |
| 111.6 | 0.235 | | |
| 152.5 | 0.307 | | |
| 153.2 | 0.308 | | |

TABLE III
Specific Heat Values for Acetone

| Crystals | | Liquid | |
|------------|-------------|-----------|-------------|
| Temp., °K. | Cp per gram | Temp., °K | Cp per gram |
| 69.9 | 0.218 | 193.2 | 0.480 |
| 74.2 | 0.227 | 196.6 | 0.480 |
| 79.9 | 0.237 | 200.1 | 0.482 |
| 85.6 | 0.248 | 210.3 | 0.485 |
| 90.8 | 0.256 | 217.5 | 0.485 |
| 91.2 | 0.258 | 276.9 | 0.505 |
| 95.2 | 0.264 | 279.3 | 0.505 |
| 100.1 | 0.271 | 283.4 | 0.507 |
| 104.3 | 0.277 | 286.4 | 0.510 |
| 105.3 | 0.280 | 289.4 | 0.510 |
| 151.2 | 0.349 | | |
| 153.0 | 0.351 | | |

¹ Parks: J. Am. Chem. Soc., 47, 338 (1925); also Parks and Kelley: J. Phys. Chem., 30, 47 (1926).

the absolute error in the experimental values is probably less than 1%. Thus in the case of iso-propyl alcohol two samples were studied with different thermocouple thermometers, lead-wire connections, etc. The results of the two sets of determinations, made over a year apart, agreed to 0.5% or better and served to indicate the reproducibility of the values obtained.

The specific heats and the fusion data, expressed in terms of the 15° calorie and with all weights reduced to a vacuum basis, appear in Tables II-IV.

TABLE IV
Fusion Data

| Substance | Melting point °K. | Heat of fusion (cal. per gram) | | |
|--------------------|----------------------|--------------------------------|-----------|-------|
| | | 1st result | 2d result | Mean |
| Iso-Propyl Alcohol | 184.6 | 21.03 | 21.14 | 21.08 |
| Acetone | 177.6 | 23.47 | 23.37 | 23.42 |

Part II: The Equilibrium Measurements

*Method.*¹ As stated before, a dynamic method was used in studying the equilibrium between iso-propyl alcohol, acetone and hydrogen in the gaseous phase. Briefly it was as follows. Pure electrolytic hydrogen, stored in a cylinder, was passed slowly thru two drying towers containing phosphorus pentoxide and then into an empty condensing tube immersed in liquid air, a precautionary device to extract impurities such as carbon dioxide or hydrocarbons; however, none of these were found. From here the hydrogen passed thru two bubblers, each containing 25 to 40 cc of iso-propyl alcohol or acetone or of a mixture of the two, depending on the direction from which the equilibrium point was being approached. These bubblers were kept at the temperature of the melting point of ice when the iso-propyl alcohol or a mixture was used and at the boiling point of liquid ammonia when filled with acetone. There were two reasons for this: first, it was desirable to have the concentrations of the iso-propyl alcohol and acetone low so that the partial pressures would follow the perfect gas law; and second, it was found by experiment that equilibrium could not be obtained with a convenient rate of gas flow if the concentrations were high. These bubblers sufficed to saturate the hydrogen with the vapor of the liquid. After saturation the gas passed into the reaction tube which will be described subsequently. Here in the presence of the catalyst the reaction took place and the resulting gaseous mixture then passed into a condensing tube immersed in liquid air, which solidified the iso-propyl alcohol and acetone. After a 1 or 2 cc sample of these had been formed by condensation (a process which took six to twelve hours), it was removed and analyzed by the refractometer method previously used by Parks and

¹ The method and results of this investigation of the equilibrium between iso-propyl alcohol, acetone and hydrogen were reported by one of us (K.K.K.) in a paper read before the chemical section meeting of the Pacific division of the American Association for the Advancement of Science at Mills College, California, June 18, 1926.

Chaffee.¹ This method involved simply the determination of the index of refraction of the sample by a Zeiss-Pulfrich refractometer. The resulting value, when referred to a chart on which we had plotted the refractive indices for known mixtures of acetone and iso-propyl alcohol against the corresponding molal compositions, gave the molal composition of the condensate sample to within 0.6%. As this analytical procedure was easy and rapid and required less than 1 cc of liquid, it was ideal for our purposes.

The Reaction Tube. The reaction tube consisted of a Pyrex U-tube about 90 cm. long and 1.2 cm. in diameter. The side thru which the reactants entered was almost completely filled with catalyst, while that thru which the products passed out was one-third full; by this arrangement the emerging gases were well removed from the catalyst before any temperature change was encountered. The reaction tube was suspended in a long Monel metal can which served as a container for the vapor bath and the boiling liquid in equilibrium therewith. This cylindrical can was wound with a heating coil and covered with sheet asbestos and a 2.5 cm. layer of "85% magnesia" insulation. The bath liquid was heated partly electrically and partly by a micro burner. The temperature of the vapor around the reaction tube was measured with a single element copper-constantan thermocouple and a White potentiometer.

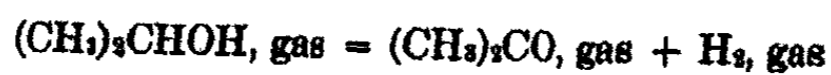
Finely divided copper was used as a catalyst, since Sabatier had found that it did not appreciably catalyze side reactions such as dehydration. This catalytic copper was prepared partly from cuprous oxide and partly from copper gauze by repeated oxidations and reductions. The first reductions were made with hydrogen and the last with iso-propyl alcohol. Air was used as the oxidizer. These repeated oxidations and reductions, about twenty in number, were made at progressively decreasing temperatures, the final one being at about 100°C. This process gave a catalyst which proved to be sensitive and made it possible to obtain the equilibrium mixture of gases from either the iso-propyl alcohol or the acetone side, altho at the lower temperatures the equilibrium point lies well over toward the alcohol side and more consistent results were always obtainable by starting from this direction.

The Equilibrium Constants. The equilibrium measurements were made by use of aniline, naphthalene and ethylene glycol as bath liquids. Of these substances the first two were very satisfactory; the ethylene glycol, however, decomposed more or less on prolonged heating with a resulting rise of the boiling point. Above 190°C. the gas entering the reaction tube consisted of either hydrogen and pure iso-propyl alcohol or of hydrogen and pure acetone. At the temperature of boiling aniline (184.3°C.), on the other hand, it was not possible to obtain equilibrium by using hydrogen and pure acetone, so a mixture of mol fraction 0.11 acetone to 0.89 iso-propyl alcohol was placed in the saturation bubblers when approaching equilibrium from the acetone side.

¹ Parks and Chaffee: J. Phys. Chem., 31, 442 (1927).

In the vapor of this mixture at 0°C. acetone was present at least to the extent of 50 mol per cent as indicated by the results of Parks and Chaffee. When equilibrium was approached from the alcohol side, hydrogen and pure iso-propyl alcohol were used as at the higher temperatures.

Under our experimental conditions all the gases involved approximate to the perfect gas behavior and their fugacities are equal to the corresponding partial pressures. Hence, the equilibrium constant for the reaction



is given by the equation, $K = P_2P_3/P_1$ where P_2/P_1 is the ratio of the partial pressures of acetone and iso-propyl alcohol and P_3 is the partial pressure of hydrogen, measured in atmospheres. The ratio, P_2/P_1 , is equal to the molal ratio of acetone to iso-propyl alcohol in the condensate and was evaluated by the refractometer analysis. The partial pressure of hydrogen was found by subtracting from the total pressure (barometric) the vapor pressure of the liquid employed in the saturation bubblers before the reaction tube, as the change in composition due to the reaction does not affect the third significant figure of the hydrogen pressure obtained in this manner. Our results appear in Tables V-IX. In all cases the prefix "a" before the number of a determination indicates that equilibrium was approached from the alcohol side and the prefix "b" that it was approached from the acetone side.

TABLE V
Equilibrium Constants at 184.3°C

| Determination | Total Pressure in mm. of Hg | P_2/P_1 | P_3 in atm. | $K = P_2P_3/P_1$ |
|------------------------|--------------------------------|-----------|------------------|------------------|
| a 1 | 765 | 0.342 | 0.997 | 0.341 |
| a 2 | 766 | 0.351 | 0.999 | 0.351 |
| a 3 | 766 | 0.406 | 0.999 | 0.406 |
| a 4 | 764 | 0.360 | 0.996 | 0.359 |
| a 5 | 764 | 0.368 | 0.996 | 0.367 |
| a 6 | 764 | 0.342 | 0.996 | 0.341 |
| a 7 | 762 | 0.360 | 0.993 | 0.357 |
| a 8 | 762 | 0.360 | 0.993 | 0.357 |
| a 9 | 762 | 0.368 | 0.993 | 0.363 |
| a 10 | 764 | 0.368 | 0.996 | 0.367 |
| Mean of the "a" values | | | | 0.36 |
| b 1 | 766 | 0.406 | 0.986 | 0.400 |
| b 2 | 766 | 0.368 | 0.986 | 0.363 |
| b 3 | 766 | 0.342 | 0.986 | 0.337 |
| b 4 | 766 | 0.389 | 0.986 | 0.384 |
| Mean of the "b" values | | | | 0.37 |

TABLE VI

Equilibrium Constants at 218.0°C

| Determination | Total Pressure in mm. of Hg. | P_2/P_1 | P_2 | $K = P_2P_3/P_1$ |
|------------------------|---------------------------------|-----------|-------|------------------|
| a 1 | 756 | 1.14 | 0.986 | 1.12 |
| a 2 | 756 | 1.14 | 0.986 | 1.12 |
| a 3 | 758 | 1.12 | 0.988 | 1.11 |
| a 4 | 758 | 1.12 | 0.988 | 1.11 |
| a 5 | 760 | 1.07 | 0.991 | 1.06 |
| a 6 | 759 | 1.14 | 0.989 | 1.13 |
| a 7 | 760 | 1.12 | 0.991 | 1.11 |
| a 8 | 766 | 1.05 | 0.999 | 1.05 |
| a 9 | 766 | 1.19 | 0.999 | 1.19 |
| a 10 | 765 | 1.17 | 0.997 | 1.17 |
| a 11 | 765 | 1.19 | 0.997 | 1.19 |
| a 12 | 765 | 1.19 | 0.997 | 1.19 |
| Mean of the "a" values | | | | 1.13 |
| b 1 | 763 | 1.17 | 0.993 | 1.16 |
| b 2 | 762 | 1.14 | 0.992 | 1.13 |
| b 3 | 762 | 1.22 | 0.992 | 1.21 |
| b 4 | 761 | 1.19 | 0.991 | 1.18 |
| b 5 | 759 | 1.14 | 0.988 | 1.13 |
| b 6 | 758 | 1.17 | 0.987 | 1.15 |
| b 7 | 756 | 1.19 | 0.984 | 1.17 |
| b 8 | 760 | 1.19 | 0.989 | 1.18 |
| b 9 | 759 | 1.18 | 0.988 | 1.17 |
| b 10 | 759 | 1.18 | 0.988 | 1.17 |
| b 11 | 759 | 1.17 | 0.988 | 1.16 |
| Mean of the "b" values | | | | 1.16 |

TABLE VII

Equilibrium Constants at a Mean Temperature of 196.4°C

| Determination | Total Pressure in mm. of Hg. | P_2/P_1 | P_2 | $K = P_2P_3/P_1$ |
|---------------|---------------------------------|-----------|-------|------------------|
| a 1 | 760 | 0.509 | 0.991 | 0.504 |
| a 2 | 760 | 0.542 | 0.991 | 0.537 |
| a 3 | 760 | 0.532 | 0.991 | 0.527 |
| a 4 | 762 | 0.542 | 0.993 | 0.538 |
| a 5 | 764 | 0.532 | 0.996 | 0.530 |
| a 6 | 763 | 0.553 | 0.995 | 0.550 |
| a 7 | 762 | 0.542 | 0.993 | 0.538 |
| a 8 | 762 | 0.542 | 0.993 | 0.538 |
| Mean | | | | 0.533 |

TABLE VIII
Equilibrium Constants at a Mean Temperature of 200.1°C

| Determination | Total Pressure in mm. of Hg. | P_2/P_1 | P_2 | $K = P_2P_1/P_1$ |
|---------------|---------------------------------|-----------|-------|------------------|
| a 1 | 762 | 0.678 | 0.993 | 0.673 |
| a 2 | 760 | 0.613 | 0.991 | 0.607 |
| a 3 | 760 | 0.587 | 0.991 | 0.582 |
| a 4 | 758 | 0.650 | 0.988 | 0.642 |
| a 5 | 762 | 0.692 | 0.993 | 0.687 |
| a 6 | 762 | 0.686 | 0.993 | 0.681 |
| a 7 | 764 | 0.667 | 0.996 | 0.664 |
| Mean | | | | 0.648 |

TABLE IX
Equilibrium Constants at a Mean Temperature of 201.8°C

| Determination | Total Pressure in mm. of Hg. | P_2/P_1 | P_2 | $K = P_2P_1/P_1$ |
|---------------|---------------------------------|-----------|-------|------------------|
| b 1 | 760 | 0.692 | 0.980 | 0.678 |
| b 2 | 760 | 0.692 | 0.984 | 0.681 |
| b 3 | 759 | 0.650 | 0.980 | 0.637 |
| b 4 | 760 | 0.664 | 0.982 | 0.652 |
| b 5 | 762 | 0.678 | 0.989 | 0.671 |
| b 6 | 759 | 0.692 | 0.987 | 0.683 |
| Mean | | | | 0.667 |

Calculations and Discussion

ΔS_{298} by the Third Law. According to the statement of the third law of thermodynamics at the beginning of this paper, the entropies of the pure crystalline acetone and iso-propyl alcohol are zero at the absolute zero. Then the entropy of each compound in the liquid state at 298° K. (i.e. 25° C.) is given by the equation,

$$S_{298} = \int_0^{298} \frac{dQ}{T} \quad (2)$$

For convenience in the calculations this may be expanded as follows,

$$S_{298} = \int_0^{70} \frac{C_P (\text{crystals})}{T} dT + \int_{70}^{T'} \frac{C_P (\text{crystals})}{T} dt + \frac{\Delta H (\text{fusion})}{T'} + \int_{T'}^{298} \frac{C_P (\text{liquid})}{T} dT \quad (3),$$

where T' is the melting point. The first integral in this expression,

$$\int_0^{70} \frac{C_P (\text{crystals})}{T} dT,$$

cannot be evaluated directly from the experimental data and therefore the "n formula" of Lewis and Gibson has been utilized for the extrapolation. By application of their methods to the data for iso-propyl alcohol, the values $n = 0.357$ and $S_{70} = 10.41$ cal./degree have been obtained. This entropy result is undoubtedly too high and possibly the absolute error in it is two or three units. However, for the purposes of a comparative study of the entropies of iso-propyl alcohol and acetone the value will be retained as given above, since without doubt the application of the Lewis-Gibson extrapolation method to this alcohol and to acetone involves comparable errors which will be largely eliminated in obtaining ΔS , the entropy increase in the reaction.

The remaining three terms on the right-hand side of Equation 3 can be evaluated with much greater certainty. The quantity ΔH (fusion)/ T' is obtainable directly from the experimental data of Table IV. The two integrals were determined graphically by plotting the values of C_P per mol as ordinates against $\ln T$ as abscissas and measuring the area under the curve. The results for both substances appear in Table X.

TABLE X
Entropy Data

| Substance | Crystals | | Entropies per mol | | S_{298} |
|--------------------|----------|-----------|-------------------|--------|-----------|
| | 0-70° | Above 70° | Fusion | Liquid | |
| Iso-Propyl Alcohol | 10.41 | 14.57 | 6.86 | 14.28 | 46.1 |
| Acetone | 14.35 | 15.90 | 7.65 | 14.76 | 52.7 |

The entropy of a mol of hydrogen is 29.4 units at 298° K. according to Lewis, Gibson and Latimer. Therefore, for the reaction $(\text{CH}_3)_2\text{CHOH}$, liquid = $(\text{CH}_3)_2\text{CO}$, liquid + H_2 , gas, $\Delta S_{298} = 52.7 + 29.4 - 46.1 = 36.0$ cal./degree on the assumption of the third law. The error in this value for ΔS is probably less than 1.5 entropy units.

ΔS_{298} from the Equilibrium Data. We shall now consider the equilibria data and compare the value for ΔS_{298} thereby obtained with the preceding one.

The rate of change of ΔH (i.e. the heat absorbed) with respect to the temperature for any reaction is given by the equation,

$$\left(\frac{\delta\Delta H}{\delta T}\right)_P = \Delta C_P \quad (4),$$

where ΔC_P in the present case is the heat capacity of one mol of gaseous acetone plus that of one mol of hydrogen minus the heat capacity of one mol of gaseous iso-propyl alcohol, since here we must consider the reaction in the gaseous phase as in the equilibria measurements. The equations for the heat capacities of acetone and iso-propyl alcohol as functions of the temperature are not known. That for hydrogen, calculated from values given by Partington and Shilling,¹ is per mol $C_P = 6.65 + 0.00070 T$. Altho the heat capacity of iso-propyl alcohol is probably somewhat larger than that for acetone, it seems reasonable on the basis of existing data for various substances to believe that the difference is not great. Therefore, in the present

¹ Partington and Shilling: "Specific Heats of Gases," p. 206 (1924).

reaction we shall take ΔC_P as equal to 4.0 calories. This procedure is admittedly somewhat arbitrary. However, it does not greatly affect our calculations of ΔS or our conclusions, as any error in ΔC_P causes practically compensating errors¹ in ΔF and ΔH . Integrating Equation 4 on this assumption for ΔC_P , we obtain the expression

$$\Delta H_T = \Delta H_0 + 4.0 T \quad (5)$$

where ΔH_0 is the constant of integration.

For the free energy change in a reaction, the following general relation exists,

$$\left[\frac{\delta(\Delta F/T)}{\delta T} \right]_P = \frac{-\Delta H}{T^2} \quad (6)$$

Substituting the value for ΔH given by Equation 5, integrating and then multiplying thru by T , we obtain the expression

$$\Delta F_T = \Delta H_0 - 4.0 T \ln T + I T \quad (7)$$

where I is the constant of integration.

The constants, ΔH_0 and I , can be evaluated by use of two values for ΔF_T obtained at different temperatures. These in the present case can be calculated from the measured equilibrium constants at the respective temperatures of boiling aniline and boiling naphthalene by means of the equation

$$\Delta F_T = -R T \ln K. \quad (8)$$

The essential data are:

$$K = 0.36 \text{ at } 184.3^\circ \text{ C. or } 457.4^\circ \text{ K.; } \Delta F = 933 \text{ cal.}$$

$$K = 1.15 \text{ at } 218.0^\circ \text{ C. or } 491.1^\circ \text{ K.; } \Delta F = -137 \text{ cal.}$$

Substituting these values of ΔF in Equation 7 and solving the two simultaneous equations, we obtain $I = -2.6$ and $\Delta H_0 = 13,310$ cal. Therefore Equations 5 and 7 become

$$\Delta H_T = 13,310 + 4.0 T \quad (9) \text{ and}$$

$$\Delta F_T = 13,310 - 9.21 T \log T - 2.6 T, \quad (10)$$

from which the changes in heat content and free energy for the reaction may be obtained at any temperature. As a check upon the validity of these equations we have also used the equilibrium constants obtained for the ethylene glycol temperatures to calculate the corresponding free energy changes (ΔF), which then afford us alternate values for I when substituted in Equation 10. For a complete consideration of the problem we have treated Rideal's data obtained by his static method in the same way. All these results appear in Table XI.

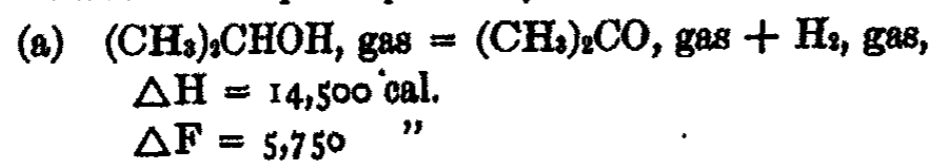
¹ Thus, for instance, we have also carried out all our calculations on the assumption that $\Delta C_P = 6.0$ cal. (an improbably high value, we believe), with the result that our final entropy change becomes 34.9, instead of 35.9 as shown subsequently.

TABLE XI
Equilibria Data and the Constant I

| | T | K | ΔF_T | I |
|------------------|-------|---------|--------------|------|
| Parks and Kelley | 457.4 | 0.36 | +933 cal. | -2.6 |
| | 491.1 | 1.15 | -137 " | |
| | 469.5 | 0.533 | +587 | -2.5 |
| | 473.2 | 0.648 | +407 | -2.7 |
| | 474.9 | 0.667 | +383 | -2.5 |
| Rideal | 378.1 | 0.00028 | +4,410 | +0.2 |
| | 423.1 | 0.0204 | +3,270 | +0.5 |
| | 448.1 | 0.177 | +1,540 | -1.8 |
| | 473.1 | 0.523 | +610 | -2.3 |
| | 498.1 | 1.35 | -300 | -2.4 |
| | 523.1 | 4.82 | -1,640 | -3.5 |
| | 548.1 | 12.0 | -2,710 | -4.0 |

Examination of the values for I shows that our data obtained by the dynamic method are very concordant and that Rideal's data over the temperature range 448°-523° K. inclusive are in fair agreement with our own. However, this is not true for his two lowest temperatures, and his result for the highest temperature is also indicative of an increasing departure from -2.6, our mean value. We believe that the correct explanation for this situation is to be found in a failure to obtain equilibrium at the lower temperatures and to secondary decomposition of the acetone at the higher temperatures. To quote his own words, "it was found in general that slight decomposition could not be avoided and that, although the decomposition curves could be repeated, the values obtained for the process of hydrogenation were by no means regular. If sufficient time were given for the system to arrive at equilibrium, secondary decomposition occurred relatively rapidly at high temperatures, and after two or three hours contact at low temperatures."

Therefore, using Equations 9 and 10, we calculate for the reaction at 298° K. and 1 atmosphere pressure,



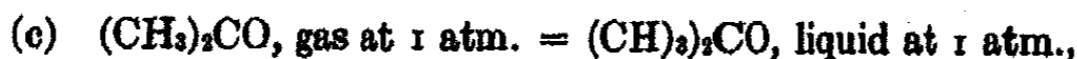
However, it is customary to take the liquid state as the standard state of iso-propyl alcohol and acetone, since that is the ordinary form for these substances at 298° K. and 1 atmosphere pressure. Now for the process,



$\Delta H_{298} = 10,620 - 300 = 10,320 \text{ cal.}$, where 10,620 cal. is the heat of vaporization¹ of iso-propyl alcohol at 25°C under its own vapor pressure, 44.0 mm. of mercury, and -300 cal. is our estimate of the Joule-Thomson effect for compressing the resulting vapor isothermally from 44 to 760 mm.; and $\Delta F_{298} = R T \ln 760/44 = 1690 \text{ cal.}$

¹ Parks and Barton: J. Am. Chem. Soc., 50, 26 (1928).

In like manner for the process,



$\Delta H_{298} = -7590 + 200 = -7390$ cal., where 7,590 cal. is the heat of vaporization¹ of acetone at 25°C under its own vapor pressure, 226.5 mm.,² and + 200 cal. is our estimate of the Joule-Thomson effect for expanding the vapor isothermally from 760 to 226.5 mm.; and $\Delta F_{298} = R T \ln 226.5/760 = -720$ cal.

Finally, combining Equations a, b and c, we obtain for the standard state reaction,



$\Delta H_{298} = 17,430$ cal.; and $\Delta F_{298} = 6,720$ cal. For the entropy change, these results give by Equation 1: $\Delta S_{298} = 35.9$ cal./degree. This value for ΔS_{298} is probably good to within 2.0 entropy units and is in excellent agreement with the result, $\Delta S_{298} = 36.0 (+1.5)$, obtained by means of the third law. While the check in the present instance is undoubtedly somewhat fortuitous, it seems reasonable to claim that this is a much better test of the third law in the case of an organic reaction than any heretofore proposed.

The Hydroquinone, Quinone Reaction

As mentioned before, the reaction,



provides us with another test of the third law.

Lange³ has determined the heat capacity of crystalline hydroquinone and quinone from liquid hydrogen temperatures up to that of the room. Without doubt his results are reasonably accurate and will serve excellently for estimating the respective entropies of these two substances at 285°K. (i.e. 12°C) on the assumption of zero entropy at zero absolute. Thus, by plotting his values for the molal heat capacity of hydroquinone against the natural logarithms of the corresponding temperatures, we obtain by graphical integration 31.3 units for the increase in entropy between 20° and 285°K. There are no heat capacity data for this substance below 20° but the work of Simon⁴ has indicated that the Debye T³ law holds for organic substances up to about 12°K and that above this point the heat capacity changes gradually so as to become at first proportional to the square of the temperature and finally, in the neighborhood of liquid air temperatures, directly proportional to the temperature. With this information we have estimated the entropy increase for hydroquinone between 0° and 20°K to be 0.8 unit per mol. Then, on the assumption of the third law, the total entropy at 285°K is 32.1 units per mol.

¹ Felsing and Durban: *J. Am. Chem. Soc.*, **48**, 2893 (1926).

² Parks and Chaffee: *J. Phys. Chem.*, **31**, 442 (1927).

³ Lange: *Z. physik. Chem.*, **110**, 350 (1924).

⁴ Simon: *Ann. Physik*, (4) **68**, 260 (1922); *Z. Physik*, **38**, 227 (1926).

In similar fashion we have estimated the entropy increase for quinone to be 1.4 cal./degree in going from 0° to 20°K. From 20° to 285°K the increase, obtained by graphical integration, amounts to 36.4 units per mol. Thus the total entropy at 285°K is 37.8 cal./degree.

As stated before, the entropy of a mol of hydrogen at 298°K is 29.4 units. C_p for hydrogen at room temperature is 6.85 cal. and hence $S_{285} = 29.4 - 6.85 \ln 298/285 = 29.1$ cal./degree. By the third law we then find for the above reaction, $\Delta S_{285} = 37.8 + 29.1 - 32.1 = 34.8 (\pm 1.0)$ cal./degree.

The electromotive force, E , and its rate of change with temperature, dE/dT , have been determined by Conant¹ and by Schreiner² for a galvanic cell involving this particular reaction. These results have not been obtained directly but represent indirect determinations from a study of the quinone-quinhydrone and the quinhydrone-hydroquinone electrodes. However, in all probability these values are very reliable, as the cells employed were reversible and reproducible. Conant obtained 0.690 volts for the e.m.f. associated with the reaction under consideration and 0.00072 for dE/dT at 285.6°K. Similarly Schreiner found $E = 0.6905$ and $dE/dT = 0.000770$ at 285°. The two values for E are in excellent agreement, altho unfortunately the respective results for the temperature coefficient differ by over 6%.

ΔS for a reaction is related to dE/dT by the simple equation

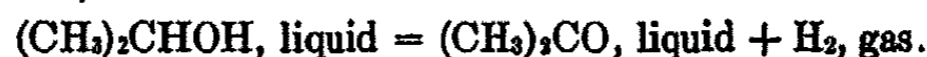
$$\Delta S = 23,074 \left[\frac{\delta E}{\delta T} \right]_p. \quad (11)$$

Hence, for this reaction $\Delta S_{285} = 33.2$ according to Conant's data and 35.5 cal./degree according to the data of Schreiner. The mean of these two results, 34.4, is probably accurate to within 2.0 units and is in excellent agreement with the value previously obtained from the heat capacity data on the assumption of the third law of thermodynamics. Thus we have here another very good check on the third law in the case of an organic reaction.

Summary

1. The present status of the proposed third law of thermodynamics has been reviewed with special reference to its applicability to organic reactions. In this connection it has been pointed out that none of the earlier tests of this principle in the field of organic chemistry may be considered adequate.

2. In view of this situation, we decided in 1923 to again test the third law, using the reaction,



Accordingly, we have measured the heat capacities of iso-propyl alcohol and acetone in the crystalline and liquid states from 70° to 298°K. We have also determined the heat of fusion of each substance at its melting point. From these thermal data ΔS_{298} has been calculated on the assumption of the third law.

¹ Conant and Fieser: J. Am. Chem. Soc., 45, 2198 (1923).

² Schreiner: Z. physik. Chem., 117, 77 (1925).

The equilibrium constants for this reaction in the gaseous phase have been measured with copper as a catalyst over the temperature range, 184°--218°C. With the aid of these results we have calculated ΔF_{298} and ΔH_{298} for the reaction involving liquid iso-propyl alcohol and acetone. The value for ΔS_{298} thereby obtained is in good agreement with that calculated from the thermal data. This check indicates the validity of the third law in the field of organic chemistry.

3. Recent data pertaining to another organic reaction,



have been utilized in obtaining a second very accurate test of the third law.

*Stanford University, California,
November 3, 1927*

THE OPTICAL SENSITIZING OF SILVER HALIDE EMULSIONS

Part I. The Adsorption of Orthochrome T to Silver Bromide

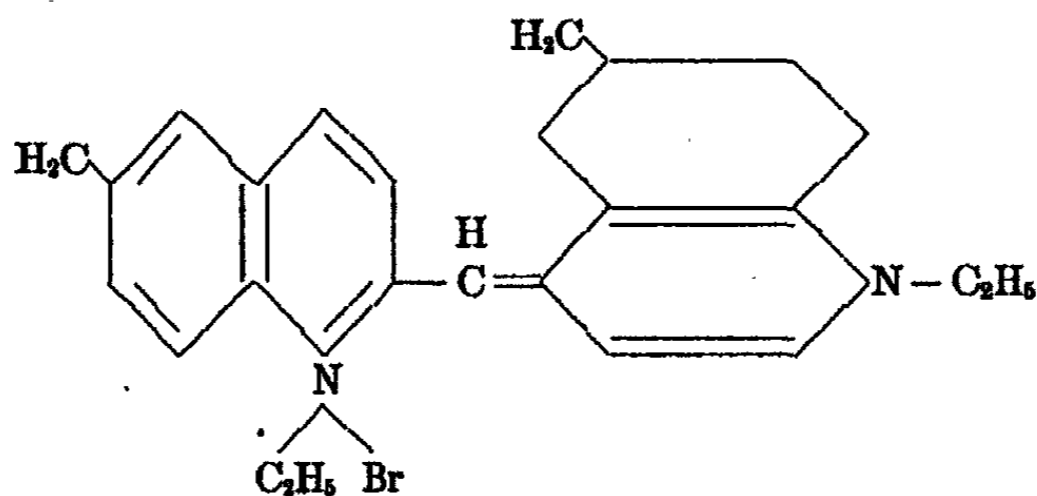
BY S. E. SHEPPARD AND H. CROUCH

Communication No. 337 from the Kodak Research Laboratories

The problem of optical sensitizing has received much attention on the practical side, and the number of valuable sensitizing dyes has been greatly extended. The theory of the action has been attacked mainly from qualitative experimental evidence, or in pure speculation, but very little quantitatively.

The first questions are, how much dye is attached to silver halide and what is the nature of the combination?

Earlier studies by one of the authors on the isocyanine dyes¹ indicated that spectrophotometric determination in non-aqueous solvents should afford a satisfactory method of estimating these dyes even in quite small amounts. A study was made therefore of the partition of an isocyanine-orthochrome T-bromide between aqueous solutions and chloroform.



The partition was measured between chloroform and both $M/20$ (.05 molar) and $M/100$ (.0066 molar) phthalate buffer solutions. In these experiments 5 cc. chloroform were shaken with 20 cc. of aqueous buffer and the dye determined spectrophotometrically. It was found that there was a large specific salt effect, in that the partition coefficients,

$$C = \frac{\text{concentration in aqueous layer}}{\text{concentration in chloroform}}$$

were much higher in the weaker buffer solutions of the same pH.

¹ S. E. Sheppard: Proc. Roy. Soc., 82A, 256 (1909).

TABLE I
Partition Coefficient

| pH | M/20 | M/150 | Water + Acid or Alkali |
|-------|------|-------|---------------------------|
| 1. | | | — |
| 2. | | | — |
| 3. | | — | 11.5 |
| 3.2 | .064 | | |
| 4.0 | | 2.7 | .14 |
| 4.05 | .013 | | |
| 5.00 | .003 | | .125 |
| 5.40 | | .89 | |
| 6.00 | .003 | | |
| 8.00 | | .10 | .03 |
| 10.00 | | | 0. |

The mechanism of this salt effect, whether a salting out effect on solubility or otherwise, requires further investigations, but is probably similar to the depression of solubility of non-electrolytes by strong electrolytes in general.

It appeared to be of interest to ascertain the effect of soluble halides on the partition between water and chloroform.

TABLE II

| Molar Ratio of Dye to Halide | Concentration of Halide | Partition of Dye in Aqueous Layer | | |
|---------------------------------------|----------------------------|--------------------------------------|------|------|
| | | NaCl | KBr | KI |
| — | .0 | .19 | .19 | .19 |
| 1:1 | .0001N | .173 | .175 | .008 |
| 1:10 | .001N | — | .040 | — |
| 1:100 | .01N | .081 | .005 | — |
| 1:1000 | .1N | .070 | — | — |

Again 5 cc. chloroform containing 0.0010 gm. dye were shaken with 20 cc. aqueous solution.

These figures may represent the relative solubilities of the chloride, bromide, and iodide dye salts, on which is superposed the isohydric depression of solubility by a common ion, but require extension to determinations at various pH values.

State in Solution and Absorption Curves

The isocyanines¹ are converted by acids into a colorless form. At any given pH there is an equilibrium between the colored and colorless forms, and this can be followed by the absorption spectra in the visible and ultra-violet.²

¹ S. E. Sheppard: J. Chem. Soc., 95, 17 (1909); Phot. J., 48, 300 (1908).

² Cf. also R. Brode: J. Am. Chem. Soc., 46, 581 (1924).

The curves in Fig. 2 show the values obtained in aqueous solution. It will be seen that as the "colorless" form increases, the ultra-violet absorption increases.

The solubility of the dye in water diminishes with increasing pH, because while the colorless form seems to be quite soluble, the colored form is very little soluble in true solution, but readily disperses to colloidal solution. In

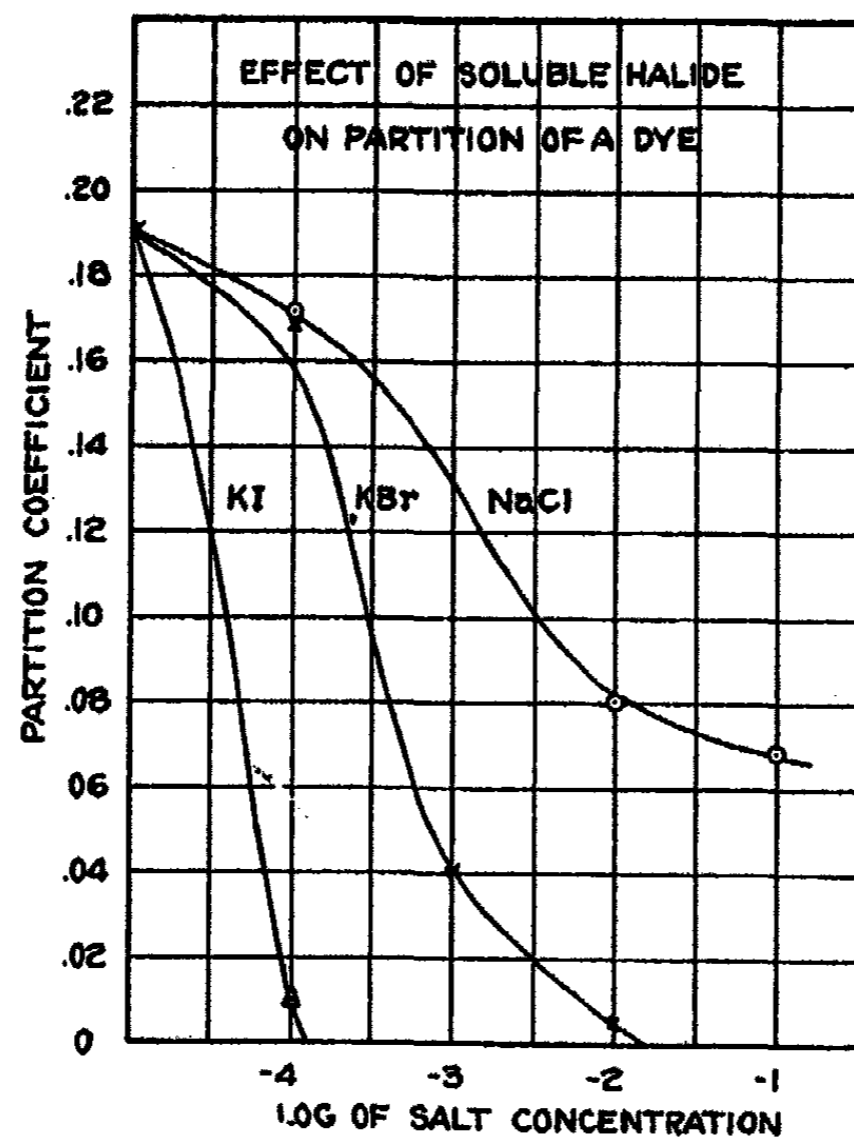


FIG. 1

acid solution the dye migrates to the cathode—corresponding to its dissociation into a large organic cation, and a halide ion. In alkaline solution (pH 13) no migration was observed in the electric field, but the experiments require extending, as the colloid micelles are probably charged. The tautomeric change is supposed to consist in the realignment of valencies in a conjugated chain of double bonds.

In organic solvents the solubility of the colored form is greater, the location of the absorption maximum slightly affected.

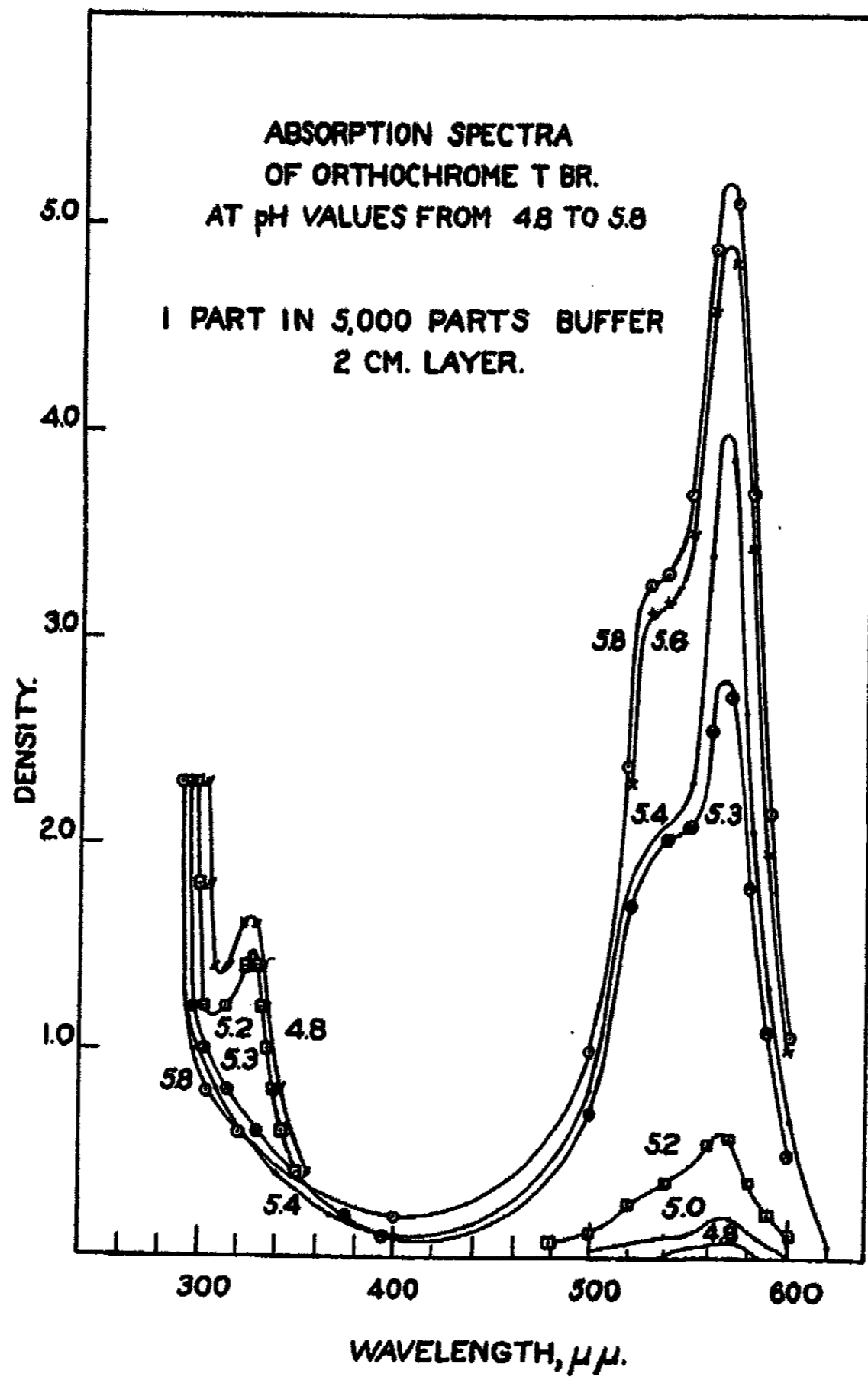


FIG. 2

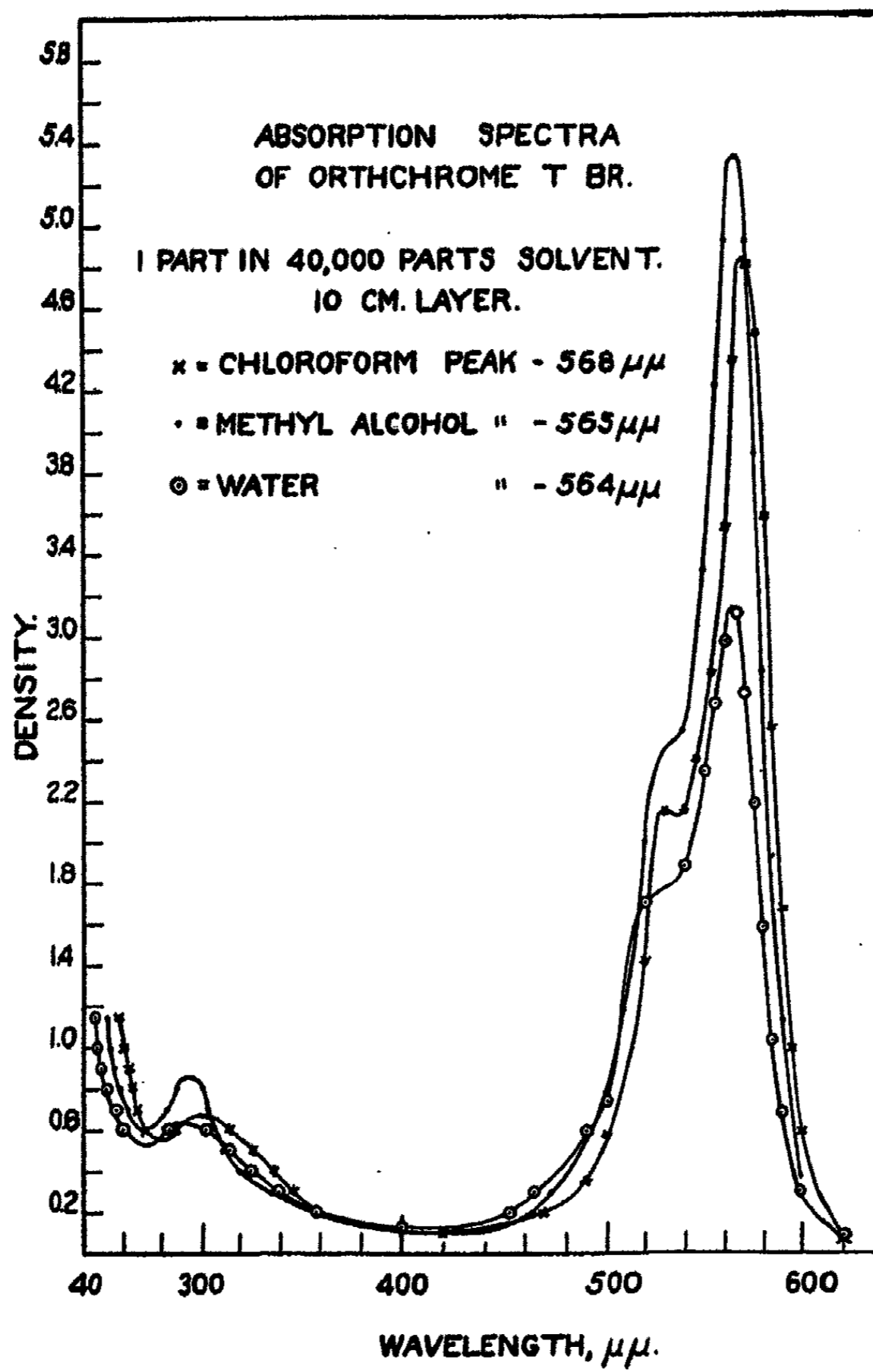
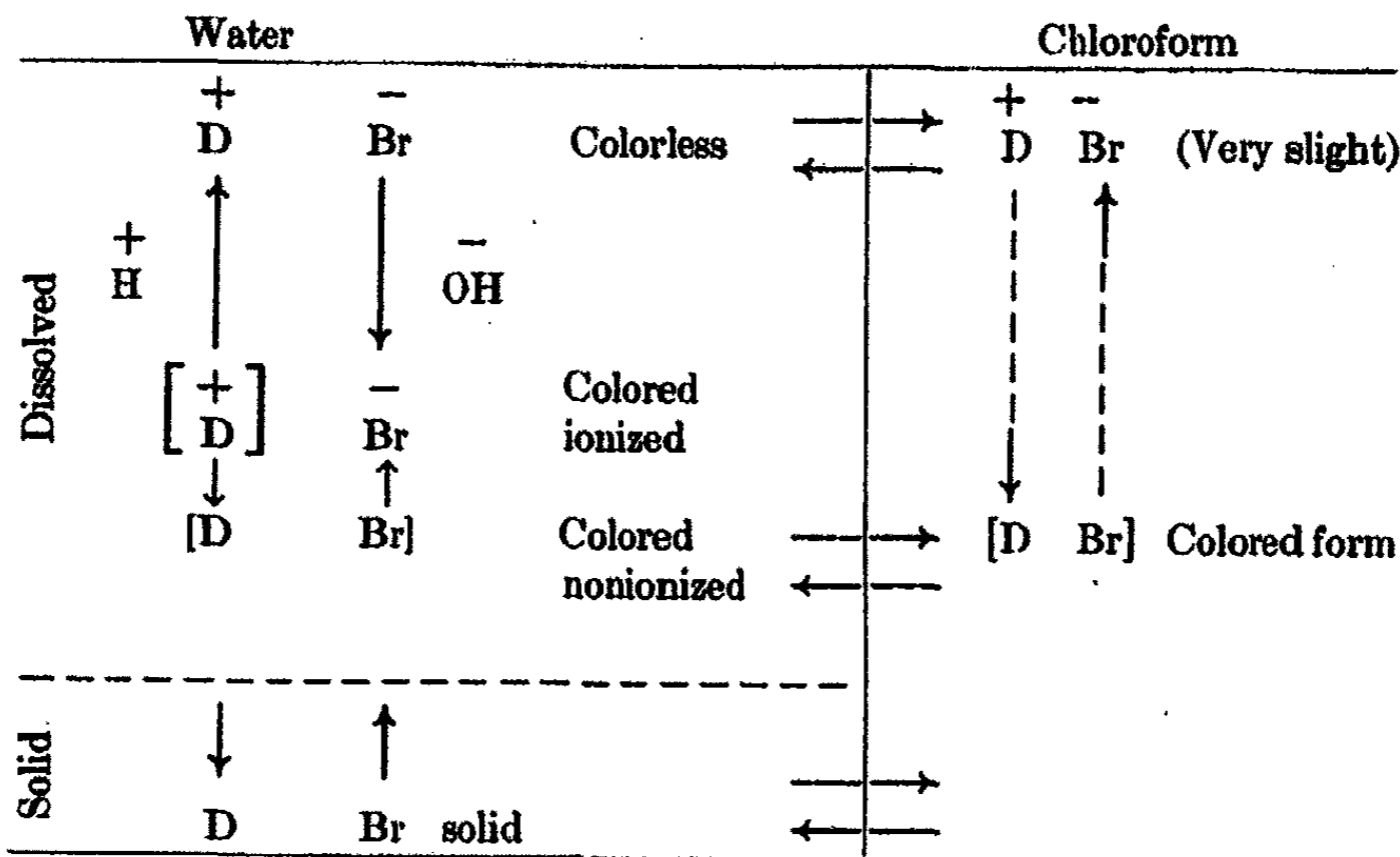


FIG. 3

It is important to note that the partitions between aqueous solutions and chloroform indicate that the colored form is very little soluble in water, and also is much less polar than the colorless form. The partition may correspond to the following equilibrium system:—



or a hydroxyl may replace bromide (Br) with increasing OH^- ion concentration. Insolubilization of the colored form by salts, and halides, would give higher concentrations of dye in chloroform. The nature of the aqueous and chloroform solutions respectively is of great importance for the adsorption and sensitizing processes.

Adsorption to Silver Bromide

The method used was as follows: A suspension of silver bromide was prepared giving microscopically measurable grains. The grain-size frequency was determined by methods already described.¹ To reduce interference of the gelatin with the dye adsorption, the adsorption experiments were carried out at 50°C , the gelatin being only 1 per cent in concentration. This procedure is not entirely satisfactory, and a method of enzyme stripping of the gelatin has been developed for use in later work. Five cc. of the silver bromide emulsion containing a known amount of the silver bromide were diluted to 25 cc. with water, adjusted to a known pH with alkali or acid, and containing a known amount of dye, were added as concentrated alcoholic solution.

The reaction system was placed in stoppered amber glass bottles in a thermostat at 50°C and shaken for one to two hours. The silver bromide was then separated by centrifuging, at about 50°C .

The residual dye in the liquid was determined by extraction with CH_2Cl_2 and spectrophotometric determination. The dye actually adsorbed to the

¹ Cf. S. E. Sheppard and A. P. H. Trivelli in Vol. III, Eder's Handbuch Phot., Part I., Lüppo-Cramer, "Die Grundlagen der photographischen Negativverfahren."

TABLE III
Data for Adsorption Curves

pH 5.5
Mixture used:
5 cc. precipitate (.4N AgBr, .08N KBr — 400 sq. cm. projective area per cc.)
20 cc. water.
1 cc. Methyl Alcohol with Dye.

| Total Dye Used Gms. | Final Concentration Gms. Kept in Sol. | Dye Adsorbed to 5 cc. Ppt. | Molecules Adsorbed per cm ² | Molarity of Dye left in Solution |
|---------------------|---------------------------------------|----------------------------|----------------------------------------|----------------------------------|
| .001 | .00039 | .00061 | 3.5 × 10 ⁻¹⁰ | .343 × 10 ⁻⁴ |
| .002 | .0012 | .00080 | 4.6 | 1.06 |
| .004 | .00313 | .000875 | 5.04 | 2.76 |
| .01 | .0068 | .00318 | 18.4 | 6. |
| .02 | .0084 | .0116 | 66.6 | 7.4 |
| .04 | .0114 | .0286 | 168. | 10. |
| .004 | .00313 | .000875 | 5.04 | 2.76 |
| .008 | .00659 | .00141 | 8.1 | 5.8 |
| .016 | .00925 | .00675 | 38.8 | 8.15 |
| .00002 | .000015 | .000005 | .03 | .0134 |
| .00005 | .000015 | .000035 | .2 | .0134 |
| .0001 | .00002 | .000080 | .46 | .0178 |
| .0002 | .000074 | .000126 | .73 | .064 |
| .0005 | .000017 | .000330 | 1.96 | .15 |
| .001 | .000556 | .000444 | 2.55 | .49 |
| .00002 | .000005 | .000015 | .09 | .005 |
| .00005 | .000014 | .000036 | .21 | .012 |
| .0001 | .000020 | .000080 | .46 | .018 |
| .0004 | .00011 | .00029 | 1.67 | .097 |
| .0008 | .00031 | .000488 | 2.81 | .274 |
| .001 | .00045 | .00055 | 3.16 | .39 |
| .001 | .00040 | .00060 | 3.46 | .35 |
| .008 | .0045 | .00352 | 20.2 | 3.96 |
| .008 | .0039 | .00418 | 23.7 | 3.42 |
| .01 | .0036 | .0074 | 42.6 | 3.2 |
| .01 | .0035 | .00755 | 43.5 | 3.1 |
| .001 | .000468 | .000532 | 3.06 | .41 |
| .001 | .000473 | .000527 | 3.03 | .42 |
| .001 | .000475 | .000525 | 3.02 | .42 |
| .008 | .00445 | .00355 | 88.5 × 10 ⁻¹⁰ | 3.9 × 10 ⁻⁴ |
| .008 | .00465 | .00335 | 92.5 | 4.1 |
| .008 | .00448 | .00052 | 89. | 4.0 |
| .01 | .00552 | .00448 | 110. | 4.9 |
| .01 | .0049 | .00510 | 97.5 | 4.35 |
| .01 | .004 | .00600 | 80. | 3.6 |
| .02 | .008 | .01200 | 161. | 7.1 |
| .02 | .0069 | .01310 | 137. | 6.1 |

TABLE III (Continued)
 Data for Adsorption Curves

pH 3.0 (HCl added)

Mixture used:

5 cc. precipitate (.4 N AgBr, .08 N KBr — 400 sq. cm. projective area per cc.)

20 cc. water.

1 cc. Methyl alcohol with Dye.

| Total Dye Used Gms. | Final Concentration Gms. Kept in Sol. | Dye Adsorbed to 5 cc. Ppt. | Molecules Adsorbed per cm ² | Molarity of Dye left in Solution |
|---------------------|---------------------------------------|----------------------------|----------------------------------------|----------------------------------|
| .00005 | .0000333 | .0000167 | .096 × 10 ⁻¹⁰ | .029 × 10 ⁻⁴ |
| .0001 | .0000762 | .0000238 | .137 | .067 |
| .0001 | .0000763 | .0000237 | .137 | .067 |
| .0002 | .0001638 | .0000362 | .208 | .144 |
| .0004 | .0003476 | .0000524 | .302 | .305 |
| .0004 | .000348 | .0000520 | .300 | .306 |
| .001 | .000812 | .0001880 | 1.08 | .715 |
| .001 | .000828 | .000172 | .99 | .73 |
| .002 | .001668 | .000332 | 1.915 | 1.47 |
| .002 | .001667 | .000338 | 1.92 | 1.47 |
| .004 | .003572 | .000428 | 2.47 | 3.14 |
| .004 | .003575 | .000425 | 2.45 | 3.14 |
| .006 | .005522 | .000478 | 2.75 | 4.85 |
| .006 | .005523 | .000477 | 2.75 | 4.85 |
| .008 | .007485 | .000515 | 2.97 | 6.6 |
| .008 | .007492 | .000508 | 2.93 | 6.6 |

pH 3.8 (HBr added)

| | | | | |
|--------|----------|----------|--------------------------|-------------------------|
| .00005 | .0000305 | .0000195 | .113 × 10 ⁻¹⁰ | .027 × 10 ⁻⁴ |
| .0001 | .0000728 | .0000272 | .157 | .064 |
| .0002 | .000167 | .0000337 | .195 | .147 |
| .0004 | .000358 | .0000413 | .238 | .315 |
| .002 | .001726 | .0002740 | 1.58 | 1.51 |
| .02 | .0165000 | .0034800 | 20. | 14.5 |
| .008 | .007632 | .000368 | 2.12 | 6.7 |
| .01 | .009689 | .000311 | 1.79 | 8.6 |
| .01 | .009609 | .000393 | 2.26 | 8.6 |
| .012 | .011472 | .000528 | 3.04 | 10. |
| .014 | .01269 | .00131 | 7.55 | 11.2 |
| .016 | .01402 | .00198 | 11.4 | 12.3 |
| .018 | .01572 | .00285 | 16.4 | 13.7 |
| .020 | .01772 | .00286 | 16.4 | 15.1 |
| .020 | .01776 | .00238 | 13.7 | 15.1 |
| .004 | .003724 | .000276 | 1.59 | 3.3 |

silver bromide was also directly determined by dissolving the silver halide in thiosulfate solution, extracting the dye with chloroform and determining with the spectrophotometer. The sum of dye extracted from silver bromide and residual dye should equal the amount of original dye, and this was fairly closely fulfilled.

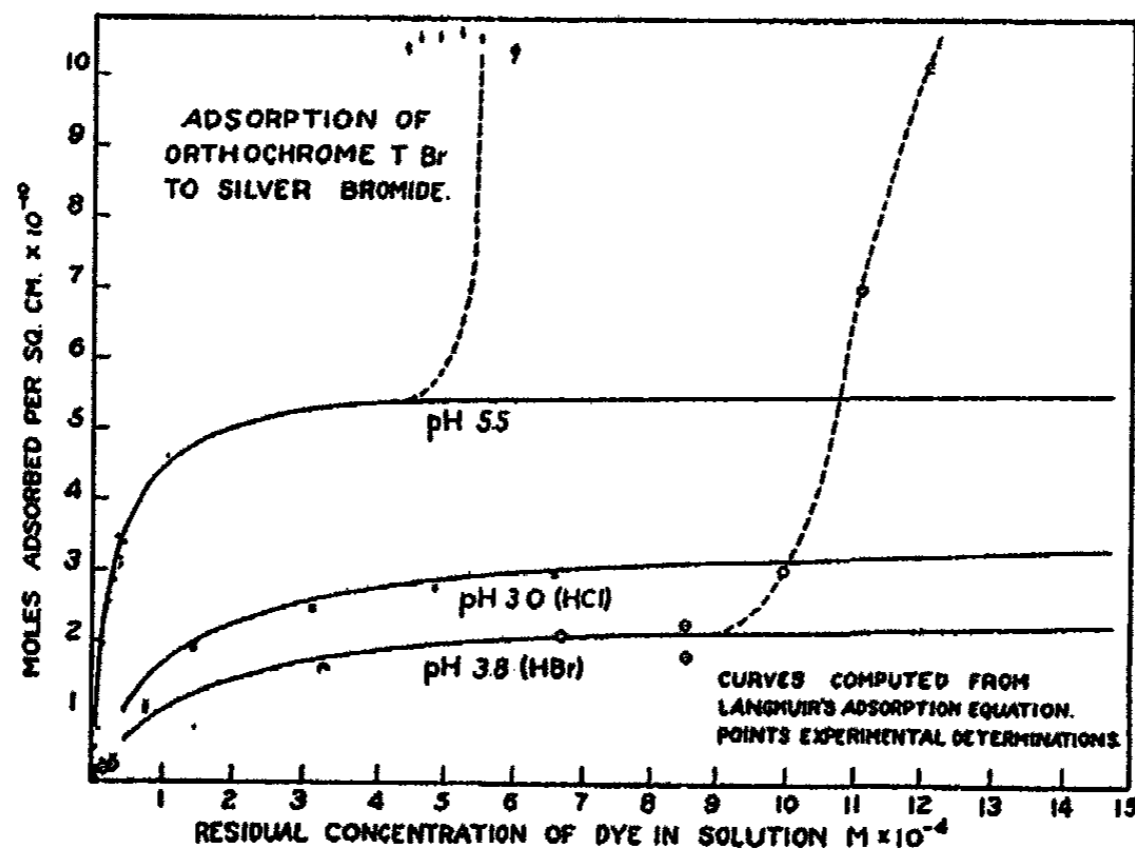


FIG. 4

Adsorption Function

The adsorption data obtained did not fit any modification of the (Freundlich) adsorption isotherm. The limit values in the horizontal part of the curves were taken as saturation values, and Langmuir's theory¹ of unimolecular layers applied in the form:

$$\eta = \frac{\tau \mu}{1 + \mu \alpha / v_1}$$

where η = gram molecules adsorbed per cm^2
 τ = average life of adsorbed molecule (time of relaxation)
 μ = gram molecules impinging on surface per cm^2 per sec.
 α = fraction of molecules which adhere
 v_1 = rate of evaporation (or solution) of molecules from surface.

Assuming $\alpha/v_1 = K$, is a constant for a given solid and adsorbant, then $\tau = n_0/NK$, where n_0 = number of atomic (molecular or ionic) spaces which can be filled

$$\begin{aligned} N &= \text{Avogadro's number} \\ &= 6.06 \times 10^{23} \end{aligned}$$

¹ J. Am. Chem. Soc., 40, 1368 (1919).

and

$$\mu = \sqrt{\frac{M}{2 \pi RT}} \cdot C = \sqrt{\frac{1}{2 \pi RTM}} \cdot C$$

$$= 1.2 \times 10^{-7} C$$

where C = concentration (\propto osmotic pressure p)
 M = molecular weight of adsorbant
 T = absolute temperature
 R = gas constant 83.2×10^6 .

The equation was used in the final form:

$$\eta = \frac{K n_0 / N \cdot \mu}{1 + \mu K}$$

From X-ray data¹ the distance between Ag and Br atoms in the lattice of AgBr is 2.89 Å.U. and the distance between centers of Br ions in an octahedral face is $\sqrt{2} \times 2.89$ Å.U. and each ion occupies 14.45 sq. Å.U. In 1 cm² surface of AgBr there are 6.93×10^{14} Br ions. From the integrated area-frequency curve the projective area per cc. of emulsion was 400 cm², and the total surface 800 cm².² Hence for 1 cc. AgBr emulsion we have $800 \times 6.93 \times 10^{14}$, i.e., 5.55×10^{17} Br ions on the surface. And at a pH 5.5 there were 5×10^{-10} gram mols dye adsorbed at saturation per cm². This gives $\frac{5 \times 10^{-10} \times 6 \times 10^{23}}{6.9 \times 10^{14}}$ molecules dye per Br ion, or 1 molecule dye per 2.3 Br ions.

Discussion

The adsorption curves obtained and the saturation values calculated are at first sight in agreement with the following theory. We may suppose that adsorption is due to the electrostatic attraction of a dye cation [D^+] to bromide anions of the AgBr surface. It has been shown by Trivelli and Sheppard³ that in AgBr crystals found in gelatin emulsions the octahedral surfaces constitute much the largest proportion. These surfaces will consist either of silver ions or bromide ions; in the presence of slight excess of bromide, of the latter.³ The limiting adsorption density would then be 1 dye cation or molecule to every bromide ion of the lattice surface.

The increase of adsorption density with pH may then be interpreted as due to increased concentration of the colored dye form, as cation. The second rapidly ascending portion of the adsorption curves, on this view, corresponds to the adsorbed dye (from molecular solution) acting at a certain density as nuclei for the precipitation of colloiddally dispersed dye. According to this, the position of the second ascending portion should approximately correspond to the true solubility of the dye in the aqueous solution of given pH.

¹ R. B. Wilsley: *Phil. Mag.*, 42, 262 (1921).

² Assuming the grains to be flat tablets.

³ "Silver Bromide Grain of Photographic Emulsions," A. P. H. Trivelli and S. E. Sheppard, *Monographs of the Theory of Photography*, No. 1, Eastman Kodak Company (1921).

Although this interpretation appears reasonable, there are certain facts not in harmony with it. From the data on partition of the dye between aqueous solutions and chloroform, it appears as if the *colored form* is very slightly, if at all, soluble, in water, and also is very little ionized. As a non-polar, or less polar form, it shows correspondingly greater solubility in chloroform. If the dye is first adsorbed to the silver bromide as ionized, colorless¹ cation, and then transformed to the colored form at the prevailing alkalinity, it is difficult to see why the adsorption should increase with increasing pH, which lowers the concentration of the colorless form. An alternative hypothesis is that the colloiddally dispersed colored form is "salted out" on to the silver bromide by the surface excess of bromide ions, and that this first proceeds to a surface saturation, as the concentration of dye is increased, and then passes over into mechanical adsorption of the colloid dye at higher concentrations. In this case also it must be supposed that preliminary "patches" of adsorbed dye act as nuclei for further precipitation and adhesion.

A more complete investigation of the aqueous solutions of the dyes, and of the adsorption process is necessary before decision between ionic-molecular and colloid adsorption can be effected. Provisionally, the former hypothesis appears the more probable.

Sensitizing

Diffusion experiments into gelatin jellies at different pH values show that the diffusion rate increases with decreased pH. Experiments were run with dye solutions adjusted to a given pH and diffusing into cylinders of gelatin jelly at the same pH. After given periods, the jelly cylinders were cut in sections, and the total dye determined in each section. The plot of dye concentration against depth gives a measure of the diffusion. The results showed that the actual amount of dye passing the cross-section of gelatin jelly *surface* was approximately constant, as measured by total area of curve, but the slope was lower, the lower the pH, indicating that the diffusivity diminished with rising pH. This agrees with the tendency of the colored form to form colloidal micelles of low diffusivity.

Since it is the colored form which actually sensitizes, sensitizing by bathing with these dyes can sometimes be most uniformly effected by bathing in an acidulated solution of the dye, then adjusting with alkali to a higher pH (*cf.* absorption curves). The diffusion experiments indicate that at a pH 5 to 8 there is some dye present in the colored form in molecular solution, but the proportion relative to colloiddally dispersed dye diminishes as pH is increased.

From rough estimates, the amount of dye adsorbed at saturation appears to be very considerably higher than the amount taken up by silver halide for optimum sensitizing.

Provisionally, the mechanism of optical sensitizing, on the basis of the theory of adsorption proposed within, is as follows: Supposing that colored dye cation is electrostatically held to bromide ion, but that this original electrostriction passes into homopolar combination, in agreement with the con-

¹ That is, visibly.

clusion that the colored form is notably less polar than the colorless, on absorption of light by this in its own absorption region¹ an electron is freed, possibly from the bromide ion, and a silver ion reduced, or indirectly by the "reduced" dye cation.

This mechanism would give only one Ag atom for each dye molecule adsorbed to the silver halide. Recently² Leszynski has published evidence that (with erythrosin) up to 20 silver atoms may be photochemically reduced per dye molecule acting as sensitizer. He suggests that the photoelectron may travel some distance through the silver halide crystal, and effect a chain reaction of rather high efficiency, or that the reduced silver continues to act as an optical sensitizer.

As an alternative to this, it may be suggested that in the photodecomposition of adsorbed dye on silver bromide, the dye molecule is practically exploded with release both of several free electrons, and also of very active free radicals. The photochemical efficiency might then be considerably greater than unity, but would probably be a pronounced function of the *intensity* of the illumination.

That the optical sensitizing is connected with the photodecomposition of the dye is supported by the fact that the addition of silver ions to aqueous solutions of the dye greatly accelerates its decomposition (bleaching) by light. Our experiments on this indicated that below a molar ratio of about 1.5 Ag⁺ to 1 mole dye, little or no acceleration of decomposition was produced, while from this point the acceleration was approximately proportional to the silver concentration. Whether the apparent threshold is significant or not has not yet been determined.

Rochester, N. Y.,
January 9, 1928.

¹ Modified by the deformation effect of adsorption to silver bromide. Cf. Fajans: *Z. Electrochemie*, 28, 499 (1922).

² *Z. wiss. Phot.*, 24, 261 (1926).

THE BEHAVIOR OF DEAMINIZED GELATIN*

BY Z. C. LOEBEL**

According to the modern view, a protein is an amphoteric electrolyte capable of combining with hydrogen ion at the terminal amino groups and at the polypeptid linkages; and capable of neutralizing hydroxyl ion at the terminal carboxyl groups and at the polypeptid linkages. Recent investigations,^{1,2} have pointed to the close relationship between the properties of the proteins and their state of combination with acid and base.

The study of many of the properties of gelatin as a function of hydrogen ion concentration indicates a point of abrupt change occurs at its iso-electric point, pH 4.7. Thus at pH 4.7 there is a minimum of solubility, osmotic pressure, swelling, viscosity at 25°C., potential difference, optical rotatory power at and above 27½°C, and absorption of light; a maximum is found at this point for foaming and optical rotation below 27½°C. In 1922 Wilson and Kern² found that the swelling of buffered gelatin solutions gave a swelling-pH curve with a second minimum at pH 7.7. A second point*** of abrupt change has been found for other properties too; and the work of Davis and Oakes⁴ indicates a shift of the minimum for viscosity at 40°C from 4.7 at 25°C to about 8.0.

It was thought that an investigation of the behavior of gelatin, on whose molecular structure the free amino groups had been replaced by less reactive hydroxy groups might throw further light on the physical chemistry of the proteins. Such an alteration of the structure of the gelatin molecule should change its chemical and physical properties in a definite and measurable manner.

Materials Used

In all the experiments "Putmann's Silver Label" gelatin was used as a source of ordinary and deaminized gelatin.

The sodium nitrite, glacial acetic acid, ammonium sulphate, sodium hydroxide and hydrochloric acid used were of the ordinary C. P. variety and the two dyes for the iso-electric point experiment were used as received from the manufacturer.

The Preparation of Deaminized Gelatin****

Introductory

When a protein such as gelatin is treated with nitrous acid there is an evolution of nitrogen, presumably from the reaction of the nitrous acid with the

*Contribution from the Department of Chemistry, Columbia University, No. 565. Presented at the Philadelphia (1926) meeting of the American Chemical Society.

** This communication is an abstract of a thesis submitted by the author in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Columbia University.

*** The two points always occur as geminated points: either both are maxima or both are minima.

**** The term "deaminized gelatin" as hereinafter used, refers to the gelatin which has undergone the nitrous acid treatment.

amion groups of the protein, the amino nitrogen being replaced by hydroxy groups. This reaction forms the basis of the Van Slyke method for the quantitative estimation of amino nitrogen. Nitrous acid was first used as a deaminizing agent for proteins in 1885 by Loew.⁶ Skraup⁷ and his co-workers have been largely responsible for perfecting the methods used in preparing deaminized proteins.

In 1914 Blasel and Matula⁸ deaminized gelatin according to Skraup's method and showed by hydrogen electrode measurements that the deaminized protein was still capable of combining with hydrochloric acid. Recently Hitchcock⁹ has published a quantitative study of the acid-combining capacity of ordinary and deaminized gelatin. He prepared the deaminized product by Skraup's method, but omitted the heating on the water-bath, a preliminary study indicating that the higher temperature induced a slight hydrolysis. Analysis of Hitchcock's preparation showed an exact agreement between the difference of the total nitrogen for ordinary and deaminized gelatin, and the amino nitrogen removed in the Van Slyke analysis; in each case 0.00040 equivalents of nitrogen per gram. Furthermore, the difference between the maximum combining capacity of the ordinary and the deaminized products for hydrochloric acid was nearly equivalent to the loss in amino or total nitrogen in the deaminization.

Procedure

The deaminized gelatin was prepared after Hitchcock's method,⁹ brought to pH 4.0, dehydrated with alcohol, ground in a pebble mill, and passed through a 60-mesh sieve. The final product was left exposed to the atmosphere for a day to allow it to reach equilibrium with atmospheric moisture. It was a canary yellow, fibrous, solid and swelled in cold water like gelatin.

Analysis of the final product for total nitrogen by the Kjeldahl method gave 17.38 per cent while the original gelatin contained 17.96 per cent; a loss of 0.58 per cent or 4.1×10^{-4} equivalents per gram absolutely dry weight.

Ordinary iso-electric ash-free gelatin was prepared according to the method of Loeb,¹ ground in a pebble mill for 24 hours, passed through a 60 mesh sieve and left exposed to the atmosphere for a day to reach equilibrium with the atmospheric moisture.

The moisture in all samples of ordinary and deaminized gelatin was determined by heating in a 105° oven over night and all weights are reported on this moisture-free basis.

Determination of the Iso-electric Point of Deaminized Gelatin by the Dye Technique

Loeb¹ has shown that protein can combine with cations only on the alkaline side of its iso-electric point, and with anions only on the acid side. Hence deaminized gelatin should combine with the colored cation of a basic dye on the alkaline side, and the colored anion of an acid dye on the acid side of its iso-electric point. The iso-electric point as determined by the dye technique for gelatin, collagen and deaminized collagen shows good agreement with the values obtained by other methods.

TABLE I

| Determination of Iso-Electric Point of Deaminized Gelatin | | |
|-----------------------------------------------------------|------------|----------------|
| Acid Black | Fuchsin | pH of solution |
| Deep Blue | 'Yellow | 3.6 |
| "Green | 'Yellow | 3.8 |
| "Green (slight) | Reddish | 4.0 |
| 'Yellow | Red (deep) | 4.2 |

'—color of deaminized gelatin.

"—due to yellow of deaminized gelatin plus the blue of the dye.

Employing the dye technique as used by Thomas and Kelly²³ for collagen, the results given in Table I were obtained with Acid Black as acid dye and Fuchsin as basic dye.

These results indicate the iso-electric point to be at pH 4.0, checking the value obtained by Hitchcock⁹ for minimum of osmotic pressure.

Method of effecting Solutions

It was found that, because of the color and the turbidity of the solutions, a concentration below 0.5 per cent would be necessary in order to make optical rotation readings. It was planned to compare the different properties at a constant concentration and after a preliminary study, 0.4760 per cent was found most satisfactory.

The solutions were made up as follows: To 0.4760 gms. of sample in a 100 cc. standard flask, 10 cc. of distilled water were added, then varying amounts of acid or alkali and finally enough distilled water to reach the 100 cc. mark. After remaining at room temperature for one hour to allow the sample to swell, the flask was placed in a water-bath at either 50°C or at 75°C for five minutes, removed, inverted slowly five times and replaced in the same bath for fifteen minutes. The flask was then kept in a 25°C water-bath for ten minutes and was ready for use.

All pH values recorded in this report were obtained with the aid of a saturated KCl-calomel half cell junction with the solution being effected through a saturated salt bridge. pH was calculated from the equation, $\text{pH} = (E - 0.2466)/0.000198T$. Measurements were made at room temperature, which was recorded in each case.

Viscosity of Deaminized Gelatin

It will be recalled that Loeb's¹ viscosity-pH curves of gelatin at 25°C indicate a minimum of viscosity at the iso-electric point, pH 4.7. The viscosity-pH curves of Davis, Oakes and Brown³ at 25°C indicate no minimum at pH 4.7 while the viscosity-pH curves of Davis and Oakes⁴ at 40°C give no minimum at 4.7 but give one at about 8.0. Loeb's solutions were effected by heating to 45°C for ten minutes. Hitchcock¹⁴ found the viscosity-pH curve of gelatin at 40°C (solution effected by heating to 40°C) to be similar to that obtained by Loeb, with a minimum at pH 4.7.

Blasel and Matula⁸ measured the viscosity of deaminized gelatin but no valid conclusions can be drawn from their results because their observations were made at such wide intervals of pH.

Two groups of experiments on viscosity of deaminized gelatin were performed; in the first the solution was effected at 50°C and in the second the solution was effected at 75°C. In the first group, 5 cc. of each solution was pipetted into three Ostwald viscosimeters which were placed, respectively, into water-baths regulated at 10°C, 25°C and 50°C ($\pm 0.1^\circ\text{C}$), and after fifteen minutes the viscosities were measured. In the second the same procedure was followed except that the determinations at 10°C were omitted.

TABLE II
Viscosity of Deaminized Gelatin Solutions at Varying Temperatures
and Hydrogen Ion Concentrations
Concentration of deaminized gelatin—0.4760%
Solution effected at 50°C

| pH | $v_{10^\circ\text{C}}$ | $v_{25^\circ\text{C}}$ | $v_{50^\circ\text{C}}$ | pH | $v_{10^\circ\text{C}}$ | $v_{25^\circ\text{C}}$ | $v_{50^\circ\text{C}}$ |
|-----|------------------------|------------------------|------------------------|------|------------------------|------------------------|------------------------|
| 1.4 | 2.695 | 1.312 | 0.7915 | 6.5 | 3.849 | 2.448 | 1.506 |
| 1.9 | 2.746 | 1.542 | 0.9123 | 6.9 | 3.801 | 2.435 | 1.436 |
| 2.7 | 3.222 | 1.791 | 1.036 | 7.3 | 3.770 | 2.406 | 1.403 |
| 2.9 | 3.316 | 1.836 | 1.050 | 7.6 | 3.771 | 2.418 | 1.417 |
| 3.3 | 3.199 | 1.654 | 0.9538 | 7.9 | 3.774 | 2.442 | 1.421 |
| 3.6 | 2.871 | 1.452 | 0.8578 | 8.4 | 3.698 | 2.397 | 1.405 |
| 3.9 | 2.692 | 1.217 | 0.7251 | 8.8 | 3.511 | 2.239 | 1.334 |
| 4.0 | Turbid | Turbid | Turbid | 9.1 | 3.365 | 2.127 | 1.256 |
| 4.3 | 2.866 | 1.240 | 0.7275 | 9.6 | 3.207 | 2.045 | 1.175 |
| 4.6 | 3.104 | 1.427 | 0.8282 | 10.4 | 3.055 | 1.970 | 1.120 |
| 5.0 | 3.457 | 1.775 | 1.055 | 10.7 | 2.968 | 1.958 | 1.118 |
| 5.7 | 3.765 | 2.309 | 1.322 | 11.6 | 2.384 | 1.440 | 0.8863 |
| 6.2 | 3.800 | 2.396 | 1.456 | | | | |

TABLE III
Viscosity of Deaminized Gelatin Solutions at Varying Temperatures
and Hydrogen Ion Concentrations
Concentration of deaminized gelatin—0.4760%
Solution effected at 75°

| pH | $v_{25^\circ\text{C}}$ | $v_{50^\circ\text{C}}$ | pH | $v_{25^\circ\text{C}}$ | $v_{50^\circ\text{C}}$ |
|-----|------------------------|------------------------|------|------------------------|------------------------|
| 1.5 | 1.198 | 0.7251 | 6.5 | 2.002 | 1.199 |
| 2.3 | 1.357 | 0.8128 | 7.0 | 1.978 | 1.185 |
| 2.9 | 1.411 | 0.8389 | 7.3 | 1.965 | 1.169 |
| 3.3 | 1.367 | 0.8199 | 7.4 | 1.995 | 1.182 |
| 3.7 | 1.264 | 0.7465 | 7.9 | 2.000 | 1.185 |
| 4.0 | 1.179 | 0.7038 | 8.3 | 1.933 | 1.175 |
| 4.4 | 1.269 | 0.7276 | 9.2 | 1.861 | 1.118 |
| 4.7 | 1.361 | 0.7998 | 9.9 | 1.754 | 1.050 |
| 5.5 | 1.787 | 1.066 | 10.3 | 1.752 | 1.051 |
| 5.9 | 1.872 | 1.113 | 11.0 | 1.520 | 0.9123 |
| 6.2 | 1.987 | 1.190 | | | |

The results are given in Tables II and III and plotted in Fig. 1. The viscosity is reported as "Viscosity Ratio" V_t :

$$V_t = \frac{\text{Time in seconds at temperature } t \text{ for deaminized gelatin}}{\text{Time in seconds at } 25^\circ\text{C for water}}$$

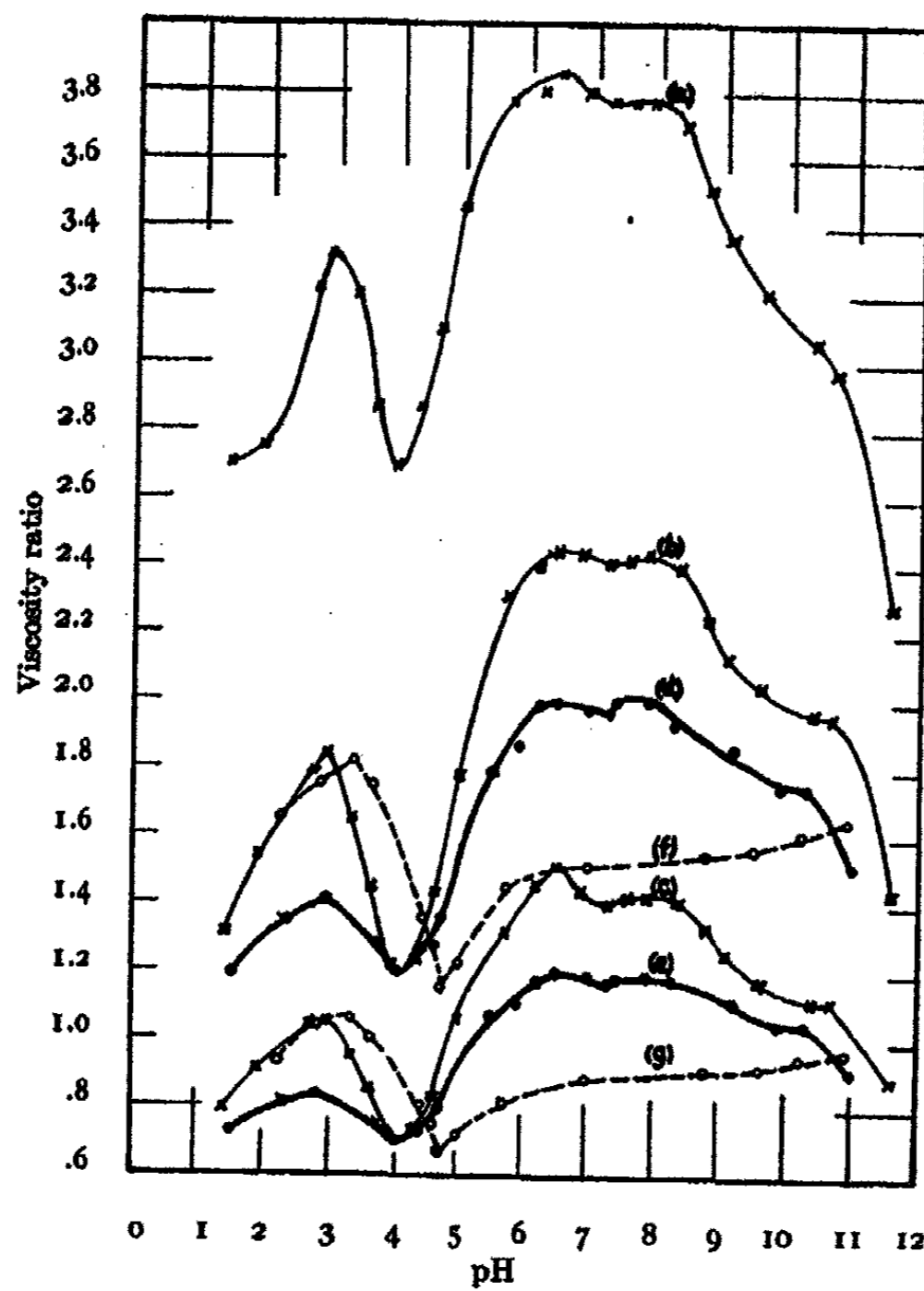


FIG. 1
0.4760% solutions of:

- *Deaminized Gelatin—Solution effected at 50°C. Viscosity at (a) 10°C, (b) 25°C, (c) 50°C
- Deaminized Gelatin—Solution effected at 75°C. Viscosity at (d) 25°C, (e) 50°C
- °Gelatin—Solution effected at 75°C. Viscosity at (f) 25°C, (g) 50°C

Although turbidity at pH 4.0 of solutions effected at 50°C permitted no viscosity measurements at this point, the direction of the curves on both sides shows a distinct tendency to locate the minimum at this point.

It will be noted further that:

- (a) Each curve, whether the solutions were effected at 50°C or 75°C, or whether the viscosities were determined at 10°C, 25°C, or 50°C, is similar in shape.

- (b) Each has a minimum at its iso-electric point, pH 4.0
- (c) In each the rise on the alkaline side is greater than on the acid side.
- (d) Each has a second minimum at pH 7.3.
- (e) Each has maximums at pH 2.9, 6.5 and 7.9.

In Table IV and Fig. 2 are given the results of a series of experiments with gelatin solutions at 25°C and 50°C, which were of the same concentration as those of the deaminized gelatin described above (0.4760%). The solutions were effected at 75°C, the same technique as used for the viscosities described being employed. These curves and the curves found by Loeb at 25°C and by Hitchcock at 40°C show many points of similarity with those of deaminized gelatin:

(a) Each of the gelatin curves is similar in shape, independent of temperature of effecting the solution.

(b) Each has a minimum at the iso-electric point. In the deaminizing reaction amino groups are replaced by less basic hydroxy groups, and it is thus expected that with deaminization there should be a shift of the iso-electric point, to the acid side, as does occur.

TABLE IV
Viscosity of Gelatin Solutions at Varying Temperatures
and Hydrogen Ion Concentrations

0.4760% gelatin solutions
Solutions effected at 75°C

| pH | $\eta_{25^{\circ}\text{C}}$ | $\eta_{50^{\circ}\text{C}}$ | pH | $\eta_{25^{\circ}\text{C}}$ | $\eta_{50^{\circ}\text{C}}$ |
|-----|-----------------------------|-----------------------------|------|-----------------------------|-----------------------------|
| 2.2 | 1.653 | 0.9348 | 5.0 | 1.226 | 0.7204 |
| 2.8 | 1.759 | 1.041 | 5.7 | 1.446 | 0.8152 |
| 3.3 | 1.820 | 1.062 | 7.0 | 1.517 | 0.8898 |
| 3.6 | 1.749 | 1.005 | 8.8 | 1.549 | 0.9135 |
| 4.4 | 1.361 | 0.8057 | 9.6 | 1.565 | 0.9240 |
| 4.6 | 1.282 | 0.7500 | 10.2 | 1.612 | 0.9502 |
| 4.7 | 1.157 | 0.6718 | 10.9 | 1.646 | 0.9739 |

(c) With gelatin the rise on the acid side of the iso-electric point is greater than that on the alkaline side; the reverse is the case with the deaminized gelatin. Comparing the 25°C and 50°C curves, it is seen that deaminization does not affect the viscosity at the iso-electric point, but lowers it on the acid side and raises it on the alkaline side; the rise on the alkaline side being very steep.

Thomas and Foster¹⁶ report a similar steeper rise of swelling with deaminization of collagen. They suggest as a possible explanation that the hydroxy groups which have substituted the amino groups are acidic in character. This would result in the formation of a greater amount of sodium salt on addition of sodium hydroxide and thus cause greater swelling.

The same explanation may be applied to account for the anomalous behavior of viscosity with deaminization of gelatin. Einstein's theory¹ holds that the viscosity is a linear function of the relative volume occupied by the

solute in the solution. The volume size of the protein solute, according to Loeb, would be dependent upon the swelling and osmotic forces which are governed by the Donnan Theory. It has been shown by Blasel and Matula⁶ and by Hitchcock,⁹ that deaminized gelatin combines with less hydrochloric acid than does gelatin. Then, following Loeb's theory, deaminized gelatin should have a lower viscosity than gelatin on the acid side, as is actually the case. In a later section a greater base-combining capacity is shown for the deaminized product, thus accounting for the greater viscosity on the alkaline side.

(d) The maximum on the acid side of the iso-electric point for gelatin is at pH 3.2, while that for the deaminized is at pH 2.9, indicating again a shift to the acid side.

(e) The second minimum for deaminized gelatin is at pH 7.3; that of gelatin is at 7.7; showing still another shift towards the acid side. A more complete discussion of the second point of abrupt change must be left to a later section.

Optical Rotation of Deaminized Gelatin

C. R. Smith postulated that there is a close relationship between the mutarotation of gelatin and its power to jellify. Prolonged heating on a water-bath causes a gelatin solution to lose both its power to jellify and to mutarotate. Kraemer and Fanselow¹² studied the optical rotation of gelatin solutions of varying hydrogen ion concentration at different temperatures, using the mercury light as a source of illumination. Their results of optical rotation as a function of pH show a minimum both at pH 4.7 and at about pH 8.0 for temperatures of 27½°C and above, and show a maximum at the same points for temperatures below 27½°C.

It was planned to study the optical properties of deaminized gelatin and to compare them with those of ordinary gelatin.

TABLE V
Optical Rotation of Deaminized Gelatin at Varying pH and Temperatures

| pH | Negative Ventzke reading at | | | pH | Negative Ventzke reading at | | |
|-----|-----------------------------|--------|--------|------|-----------------------------|------|------|
| | 10°C | 25°C | 50°C | | 10°C | 25°C | 50°C |
| 1.4 | 7.1 | 4.3 | 3.8 | 6.5 | 5.3 | 4.5 | 4.4 |
| 1.9 | 7.1 | 4.5 | 4.0 | 6.9 | 5.4 | 4.6 | 4.4 |
| 2.7 | 6.2 | 4.8 | 4.1 | 7.3 | 5.1 | 4.6 | 4.3 |
| 2.9 | 6.2 | 4.8 | 4.1 | 7.6 | 5.1 | 4.7 | 4.3 |
| 3.3 | 6.7 | 4.6 | 4.0 | 7.9 | 5.3 | 4.6 | 4.3 |
| 3.6 | 7.3 | 4.7 | 4.0 | 8.4 | 5.2 | 4.6 | 4.3 |
| 3.9 | turbid | turbid | turbid | 8.8 | 5.2 | 4.8 | 4.3 |
| 4.0 | turbid | turbid | turbid | 9.1 | 5.3 | 4.8 | 4.3 |
| 4.3 | 7.7 | 4.8 | 4.0 | 9.6 | 5.0 | 4.6 | 4.1 |
| 4.6 | 7.6 | 4.8 | 4.0 | 10.4 | 5.3 | 4.5 | 4.4 |
| 5.0 | 6.5 | 4.8 | 4.0 | 10.7 | 5.0 | 4.6 | 4.3 |
| 5.7 | 5.4 | 4.7 | 4.1 | 11.6 | 5.1 | 4.5 | 4.4 |
| 6.2 | 5.3 | 4.5 | 4.2 | | | | |

Procedure

The solutions for the optical rotation experiments were prepared as described above, the solution being effected at 50°C. The solutions were polarized in 2.2 dm. jacketed tubes, water respectively at 10°C, 25°C and 50°C ($\pm 0.3^\circ\text{C}$) being pumped through the jackets. After 15 minutes at the proper temperatures, readings were taken. The instrument used was a Schmidt and Haensch saccharimeter, with a dichromate filter. White light was used as a source of illumination. The direct readings (negative degrees Ventzke) of 10°C, 25°C and 50°C are tabulated in Table V and plotted as a function at pH in Fig. 2.

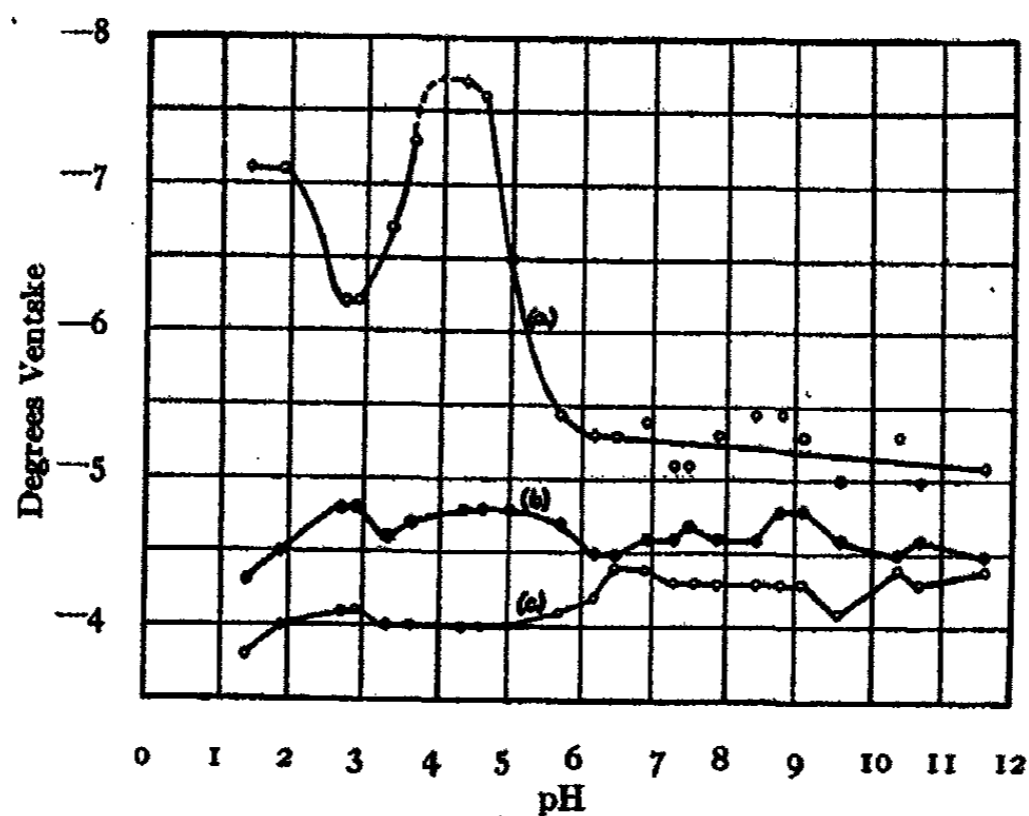


FIG. 2

Effect of temperature and pH on the optical rotation of 0.4760 per cent solution of deaminized gelatin.

- (a) = 10°C
 (b) = 25°C
 (c) = 50°C

Because of the turbidity and color no readings could be made at pH 4.0. The curve for 10°C readings shows a minimum at pH 2.9 and a tendency to form a maximum as the pH approaches 4.0. On the alkaline side of pH 4.0 the rotation falls off with increasing pH. At 25°C and 50°C the rotation is almost constant for each respective temperature. Unfortunately, the color and turbidity do not permit the use of higher concentrations which might magnify any deviations, and detect any mutarotation.

Surface Tension and Foaming of Deaminized Gelatin

Like gelatin, deaminized gelatin solutions foam on shaking. The adsorption film theory advanced by Bancroft is founded on Gibbs' statement that any substance which lowers the surface tension of a liquid must concentrate in the surface, thus forming a film and preventing the coalescence of the gas bubbles. Accordingly, gelatin and deaminized gelatin should foam most

at the points where the surface tension is least. Bogue²⁰ reports that the foaming of gelatin is a maximum at its iso-electric point. Johlin²⁶ finds its surface tension is a minimum at this point.

Surface tension

Surface tension measurements were made with the Du Nouty²⁷ tensiometer. The solutions, of 0.4760 per cent concentration, were made up by the same

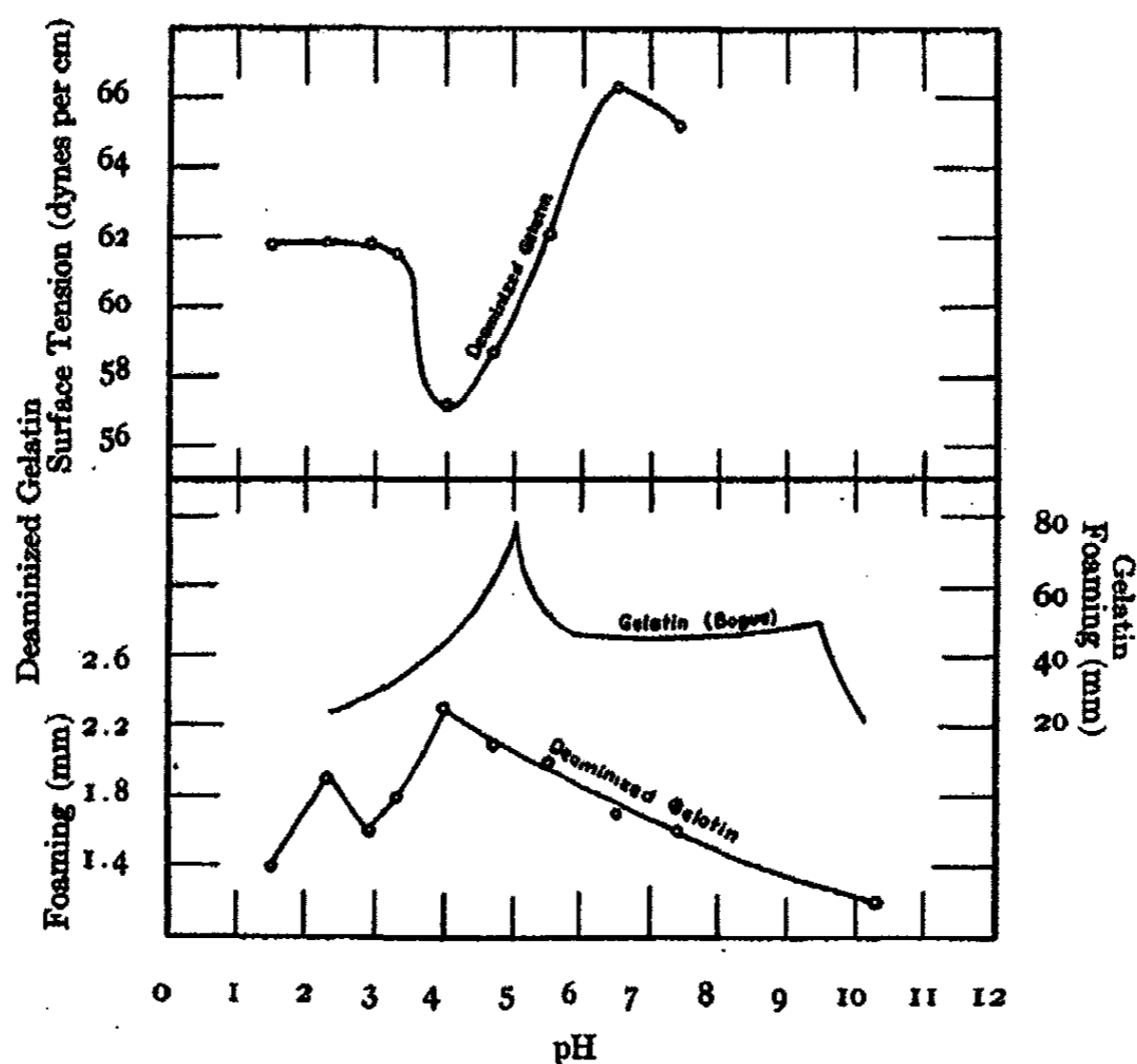


FIG. 3

Effect of pH on the surface tension of 0.4760 per cent solution of deaminized gelatin and effect of pH on the foaming of 0.4760 per cent solutions of gelatin and deaminized gelatin.

technique as described above, solution effected at 50°C. Two cc. of each solution were pipetted into respective 4 cm. watch crystals and left at room temperature for one hour. During this hour it was covered with an inverted Petri dish. Because of the exposed surface of the alkaline solutions it can not be claimed that the pH values are accurate. However, they are not sufficiently far removed to prevent the indication of the general direction of the surface tension change with pH change.

The usual precautions of flaming the pipette, watch crystals and platinum ring were taken. The apparatus was calibrated against water at 23°C giving the value of 73 dynes per cm. The results, given in Table VI and plotted in Fig. 3, indicate a minimum at pH 4.0, a maximum at pH 2.9, which remains constant with further decrease of pH; and a maximum at about pH 6.5, which remains constant with further increase of pH.

TABLE VI
Surface Tension and Foaming of Deaminized Gelatin
at Varying Hydrogen Ion Concentration

| pH | Surface Tension at 23° C Dynes/cm. | Foaming at 23° C cm. | pH | Surface Tension at 23° C dynes/cm. | Foaming at 23° C cm. |
|-----|------------------------------------------|----------------------------|------|------------------------------------------|----------------------------|
| 1.5 | 61.8 | 1.4 | 4.7 | 58.7 | 2.1 |
| 2.3 | 61.8 | 1.9 | 5.5 | 62.1 | 2.0 |
| 2.9 | 61.8 | 1.6 | 6.5 | 66.3 | 1.7 |
| 3.3 | 61.5 | 1.8 | 7.4 | 65.2 | 1.6 |
| 4.0 | 57.2 | 2.3 | 10.3 | | 1.3 |

The foaming experiments were performed with the same solutions. Ten cc of each solution was added to respective 15 cc graduated test tubes and shaken all together, and the volume of foam read off. The results are recorded in Table VI and plotted in Fig. 3. They show a maximum at pH 4.0 and a minimum at pH 2.9. The curve obtained by Bogue is inserted for comparison. Although absolute values cannot be compared here, the general trend of the two curves show several interesting differences. Both curves show a maximum at their respective iso-electric points, but the gelatin curve has a second maximum on the alkline side, while the deaminized gelatin has the corresponding maximum on the acid side.

It will be noted that the surface tension in each case is lower than that of water and that the greatest lowering point of the surface tension curve is at the iso-electric point and corresponds with the highest point of foaming. These results are in conformity with the adsorption film theory, and are similar to those of Bogue and of Johlin for gelatin.

Titration of Gelatin and Deaminized Gelatin with Sodium Hydroxide

In a preceding section it was pointed out that the increase of viscosity on the alkaline side of the iso-electric point with deaminization is very likely due to the acidic nature of the hydroxy groups¹⁶ that replaced the amino groups. If this is true, the base-combining capacity of deaminized gelatin should be greater than that of gelatin by an amount equivalent to the replacing hydroxy groups.

To obtain comparable results both gelatin and deaminized gelatin were titrated. Samples equal to 0.4617 gm. absolutely dry weight were used; varying amounts of 0.1012N sodium hydroxide added and the pH determined electrometrically. A single sample was employed for each titration curve, the original volume being 25.30 cc. Preliminary results indicated that to adjust the pH of gelatin and deaminized gelatin to pH 7.0 required respectively 1.43 cc and 3.01 cc of the sodium hydroxide used. To keep the volumes at pH values above 7.0 more nearly constant, 1.58 cc (the difference between 3.01 and 1.43) of water was added to the gelatin sample.

The results are given in Table VII and plotted in Fig. 4.

TABLE VII
Titration of Gelatin with NaOH
Weight of gelatin sample 0.4617 gm. (dry weight).

| cc. 0.1012N NaOH added | cc. 0.1N NaOH required* | Volts E.M.F. | pH | cc. 0.1012N NaOH added | cc. 0.1N NaOH required* | Volts E.M.F. | pH |
|------------------------|-------------------------|--------------|------|------------------------|-------------------------|--------------|-------|
| 0.0 | | 0.5151 | 4.58 | 1.75 | 1.62 | 0.8722 | 8.98 |
| 0.15 | 0.0 | 0.5216 | 4.70 | 1.90 | 1.77 | 0.8737 | 9.69 |
| 0.55 | 0.40 | 0.5457 | 5.11 | 2.45 | 2.33 | 0.8755 | 10.74 |
| 0.95 | 0.81 | 0.5721 | 5.56 | 3.25 | 3.14 | 0.9231 | 11.56 |
| 1.15 | 1.01 | 0.5843 | 5.77 | 3.95 | 3.85 | 0.9412 | 11.86 |
| 1.35 | 1.21 | 0.6274 | 6.51 | 5.15 | 5.06 | 0.9500 | 12.01 |
| 1.55 | 1.42 | 0.6996 | 7.74 | 8.15 | 8.10 | 0.9543 | 12.09 |
| 1.65 | 1.52 | 0.7406 | 8.44 | | | | |

*cc of exactly 0.1N NaOH required to adjust pH from 4.70 to that recorded in the last column.

TABLE VIII
Titration of Deaminized Gelatin with NaOH
Weight of deaminized gelatin sample 0.4617 gm. (dry weight).

| cc. 0.1012N NaOH added | cc. 0.1N NaOH required* | Volts E.M.F. | pH | cc. 0.1012N NaOH added | cc. 0.1N NaOH required* | Volts E.M.F. | pH |
|------------------------|-------------------------|--------------|------|------------------------|-------------------------|--------------|-------|
| -0.10** | 0.0 | 0.4806 | 4.00 | 3.20 | 3.35 | 0.7540 | 8.67 |
| 0.0 | 0.10 | 0.4834 | 4.05 | 3.55 | 3.69 | 0.8330 | 10.02 |
| 0.10 | 0.20 | 0.4860 | 4.09 | 4.00 | 4.15 | 0.8912 | 11.02 |
| 0.70 | 0.81 | 0.5052 | 4.42 | 4.20 | 4.35 | 0.8993 | 11.15 |
| 1.51 | 1.63 | 0.5340 | 4.91 | 4.50 | 4.65 | 0.9100 | 11.34 |
| 2.00 | 2.12 | 0.5533 | 5.24 | 4.99 | 5.15 | 0.9202 | 11.51 |
| 2.51 | 2.64 | 0.5745 | 5.60 | 5.50 | 5.67 | 0.9311 | 11.70 |
| 2.70 | 2.83 | 0.6010 | 6.06 | 7.50 | 7.69 | 0.9421 | 11.89 |
| 2.80 | 2.93 | 0.6065 | 6.15 | 10.50 | 10.73 | 0.9501 | 12.02 |
| 3.10 | 3.24 | 0.6718 | 7.45 | 14.50 | 14.77 | 0.9561 | 12.13 |

*cc of exactly 0.1N NaOH required to adjust pH from 4.00 to that recorded in the last column.

** 0.10 cc 0.1N HCl required.

Examining the slopes of the first part of each curve, rising from their respective iso-electric points, it is seen that the slope of the curve for the deaminized sample is steeper.

This first portion of the curve for the deaminized gelatin rises to a higher value than that of the gelatin, indicating that the hydroxy groups begin to combine with sodium hydroxide directly beyond the iso-electric point. The sudden rise in viscosity directly beyond the iso-electric point is thus accounted for.

There is a change of slope at pH 7.5 for the deaminized gelatin which corresponds to a similar point for the gelatin at pH 7.7; it is interesting that pH 7.7 corresponds to the second point of abrupt change of the properties of gelatin.

At pH 7.5, 0.4617 gm of deaminized gelatin combines with 3.24 cc 0.1N sodium hydroxide.

At pH 7.7, 0.4617 gm of gelatin combines with 1.40 cc 0.1N sodium hydroxide.

The difference is 1.84 cc 0.1N sodium hydroxide.

For 1 gm this difference is 4.0 cc 0.1N sodium hydroxide or 4.0×10^{-4} equivalents.

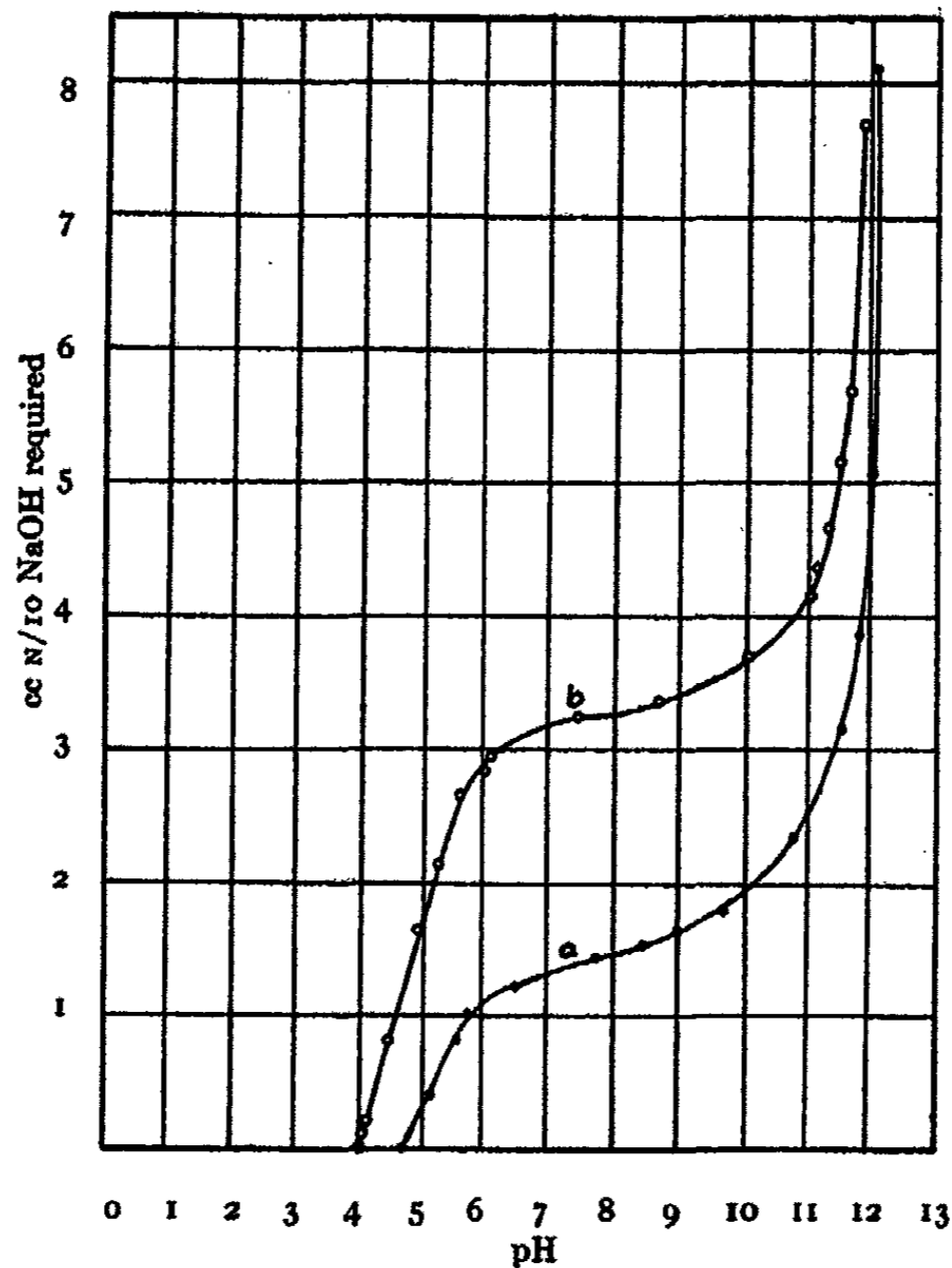


FIG. 4

Titration Curves for 0.4617 gms of originally isoelectric:

- a) Gelatin
and
b) Deaminized Gelatin with N/10 NaOH

The Kjeldahl nitrogen of the

| | |
|--------------------|------------------------------|
| gelatin | 17.96% |
| deaminized gelatin | 17.38% |
| difference | .58% or 4.1×10^{-4} |

equivalents nitrogen per gm. showing very good agreement with the difference of their base-combining capacity.

Examining the slope of the two curves beyond pH of 11, it may be seen that there exists a constant difference of about 4.0×10^{-4} equivalents of sodium hydroxide per gram dry substance. This may be construed to mean that the base-combining capacity for the deaminized gelatin is equal to that of gelatin plus 4.0×10^{-4} . Taking the value of the base-combining capacity of gelatin as found by Loeb¹¹ and Hitchcock¹⁰ at 5.7×10^{-4} , that for deaminized gelatin would be 9.7×10^{-4} equivalents per gram.

The Second Point of Abrupt Change

Several properties of gelatin, studied as a function of the hydrogen ion concentration, give curves of the same type as the viscosity curves. Some of these properties have been studied in the unbuffered range. Wilson and Kern² found a second minimum for swelling of buffered gelatin at pH 7.7. Higley and Mathews¹⁸ found a second minimum at the same point for absorption of light. Kraemer and Fanselow¹² and also Velles and Vellinger¹³ found a second point of abrupt change for optical rotation.

There seems to be only four proteins which show these double geminated points. They are collagen, deaminized collagen, gelatin and deaminized gelatin.

C. R. Smith⁷ postulated two forms of gelatin in solution, a "sol" form stable at temperatures above 35°C and a "gel" form stable at temperatures below 15°C, while at temperatures between, the existence of both in equilibrium. The work of Smith and Lloyd¹⁷ shows that the change from "gel" to "sol" form takes place with increase of Sørensen value of the solution. Wilson and Kern suggested that the two forms had different iso-electric points, the "sol" form at pH 7.7 and the "gel" form at 4.7; and that a preponderance of either one would determine the behavior.

Support for this idea is found in the work of Thomas and Kelly^{18, 19}. In studies of the rate of fixation of tannin by hide substance at room temperature¹⁸ as a function of hydrogen ion concentration of the solutions, they showed that the degree of fixation at a maximum at pH dropped to a minimum at pH 5; (the iso-electric point) rose again when a pH of about 8 was reached and then abruptly fell off with further increase in alkalinity. Since the tannin particles are negative, the decrease in rate of fixation from pH 3 to 5 was readily explained by the Procter-Wilson theory as due to the decreasing positive charge of the collagen. The rise in rate of fixation from pH 5 to 8 was unexplainable except on the basis of a shift of the iso-electric point. Thomas and Kelly¹⁹ repeating the same work at 40°C obtained no minimum at pH 5 and conclude, therefore, that the collagen exists in two modifications analogous to the "sol" and "gel" forms of gelatin; the iso-electric points of the collagen being at pH 5 and at 8.

With gelatin the evidence is more conflicting. To begin with, the exact location of the transition temperature, "gel" to "sol," is uncertain. C. R. Smith says it is at 35°C. Davis and Oakes place it at 38.03°C and Kraemer and Fanselow place it at 27½°C. Bogue,²⁰ on the other hand, says it depends on the concentration, heat treatment, pH and previous history.

Although Davis and Oakes report no minimum for the viscosity-pH curves of gelatin at pH 4.7 at 40°C and do report one at pH 8.0, it cannot be said to represent a shift of the minimum due to the temperature. Davis, Oakes and Browne using the same technique as Davis and Oakes, found the viscosity-pH curves of gelatin at 25°C gave no minimum at 4.7 either.

It was at first thought that the difference in method of effecting solution employed by Davis and his co-workers might be the cause for the difference in results. The matter was gone over with Dr. Davis and he determined the viscosities of two series of gelatin solutions, one series being treated as in his two papers—by heating on a hot plate for 20 minutes with continuous stirring till the solution reached 75°; the other series being treated in a manner similar to that employed in this research. His results indicated that the same qualitative results were obtained by either treatment.

The interpretation that has been placed on the work of Davis et al. has been that the minimum of viscosity at pH 4.7 at 25°C shifts to pH 8.0 at 40°C. Apparently the gelatin used by them did not have its iso-electric point at pH 4.7 as did that of Loeb, Hitchcock and that used in this research. Hitchcock's results for gelatin at 40°C and those reported in this investigation for gelatin and deaminized gelatin at various temperatures indicate no change of minimum with change of "gel" to "sol" form.

Loeb¹ postulated that the large changes of viscosity with pH of gelatin solutions at 25°C were due to two factors, the great magnitude of viscosity of gelatin solutions and the swollen micellae present. While such a theory is tenable enough for lower temperatures, it can hardly hold for higher temperatures, like 50°C. However, as a matter of pure speculation, it might be suggested the viscosity of gelatin is dependent upon a solution structure²¹ which in turn is dependent upon swelling forces, and therefore, according to the Donnan Theory, dependent upon osmotic force.

In the viscosity experiments of gelatin and deaminized gelatin, the solutions of which were effected at 75°C, no shift of minimum was observed. A preliminary experiment with gelatin solutions at different pH, but in which the solutions were effected by heating at 80°C for one hour, indicated no shift of the minimum.

Although the above evidence indicates no shift of the minimum of gelatin and deaminized gelatin, there is every indication of the existence of the second point of abrupt change of properties. Wilson and Kern's idea of this point as a possible iso-electric point of the "sol" form finds further support in the work of Miss Lloyd.¹⁷ She found that the "gel"- "sol" equation, brought about with increase of pH is reversible if sufficient acid is added. She offers the following explanation: "Brailsford Robertson²² has suggested that acids and bases attached themselves to protein molecules at the -COHN- linkage. He points out that this linkage may exist as an enol linkage -C-N- or as a



* Private communication.

keto linkage $\begin{array}{c} \text{---C---N---} \\ | \quad | \\ \text{O} \quad \text{H} \end{array}$ and favors the enol-form since it offers a point of

attachment to both acids and bases. A more probable explanation seems to be that under the action of acids gelatin goes over to the keto-form, and under the action of bases to the enol-form." If this theory is correct, all proteins should show these geminated points of properties. Although only four are reported to have the two points, a more extensive study should be made with the thought of their possible existence in other proteins as well.

The likelihood that the second point is the result of hydrolysis is small. Measurements by Bogue²⁰ and by Northrop²¹ show that the rate of hydrolysis of gelatin at different pH is almost a constant for the same temperature. Northrop found the rate of hydrolysis is ten times more rapid at 65°C than at 40°C. It might be argued that the iso-electric point of these hydrolytic products is at pH 7.7. However, the experiments in this research indicated no shift of the minimum of viscosity with higher temperatures.

Knaggs and Schryver¹⁶ conclude, after careful attempts in purifying gelatin to obtain a product of constant composition, that there is no reason for regarding gelatin, even after elaborate methods of purification, as a chemical entity. This suggests another possible cause for the presence of the two points as due to the predominating effect of first one group and then another group of substances present in the gelatin.

There seems to be an indication of a relationship between the chemical nature of gelatin and deaminized gelatin, and the second point of abrupt change of properties. The titration curve of gelatin with sodium hydroxide has a point on inflection at about pH 7.7, and that of deaminized gelatin at about 7.5; the former point corresponding to the point of second minimum of swelling of gelatin as found by Wilson and Kern, and the latter almost corresponding to the second minimum of viscosity of deaminized gelatin as found in this research.

However, until more experimental work is done, the cause for the existence of the second point must remain a matter of speculation.

The author expresses his appreciation to Dr. A. W. Thomas for advice and criticism during the prosecution of this investigation.

Summary

A study of the behavior of a deaminized gelatin has been made and compared with that of gelatin.

The iso-electric point of deaminized gelatin is found by the dye technique at pH 4.0. The optical rotation, viscosity, surface tension and foaming of the solutions, are studied as function of hydrogen ion concentration. The optical rotation at 10°C and the foaming at room temperature are at a maximum at the iso-electric point. Surface tension is at a minimum at this point. Whether the solutions were effected at 50°C or at 75°C, or whether the viscosities were run at 10°C, 25°C, or 50°C, the viscosity-pH curve of deaminized gelatin was of the same shape, showing two minima, at pH 4.0 and pH 7.3.

Ordinary gelatin solutions effected at 75°C gave viscosity-pH curves at 25°C and 50°C, similar to those obtained by Loeb at 25°C, with a minimum at the iso-electric point.

Titration of deaminized gelatin and gelatin with sodium hydroxide indicates that the hydroxy groups which replace the amino groups in deamination are acidic in character. The difference in the base-combining capacity of the two substances is equivalent to their difference in nitrogen content. The results indicate that the base-combining capacity of deaminized gelatin is 9.7×10^{-4} equivalents per gram.

The second point of abrupt change of properties is discussed.

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New York, N. Y.

THE ELECTROCHEMICAL BEHAVIOUR
OF SILICATE GLASSES III*
CATHODE AND ANODE GASES**

BY M. J. MULLIGAN, J. B. FERGUSON AND J. W. REBBECK

Cathode Gas

When an electric current is passed through the walls of a soda-lime glass tube containing mercury as cathode, a film of gas may form at the mercury-glass interface and once formed will disappear in time if the direction of the current be reversed. This phenomenon was first studied by Rebbeck and Ferguson¹ who found that the gas consisted of hydrogen with a little oxygen. They also determined many of the conditions essential for gas production and disappearance.

The process of gas disappearance is such a curious one that a photographic record was made in order to dispel any illusions there might be in regard to the true nature of it. Marks were etched on the outer surface of several tubes and the marked parts were photographed at different stages of the electrolysis. When the bubbles were in focus, the marks were not and hence appeared blurred in the photographs. One series of these is shown in Plates I to IV. This series was taken by Ferguson and Ellis.²

The plates show that upon current reversal the individual bubbles became smaller and some disappeared entirely. The reappearance of the gas indicated by Plate IV seems to be in no way related to the original gas film. During this stage of the electrolysis a number of chemical reactions take place. These will be discussed in a later paper on the formation of solid electrolytic deposits in glass.

The disappearance of gas on current reversal may in part be explained on the assumption that the sodium enters the glass from the sodium hydroxide film which was formed at the interface during the evolution of gas and that the water was re-formed and sorbed by the glass. In support of this suggestion, we found that hydrogen gas will disappear in the presence of sodium hydroxide but not in its absence. Bubbles of pure dry hydrogen were trapped between the mercury and the glass during the filling of a new soda-lime glass tube with mercury by distillation³ and the tube electrolysed, mercury anode, with 110 volts at 100°C for 70 hours. The gas did not disappear. A similar tube was

* Contribution from the Department of Chemistry, University of Toronto.

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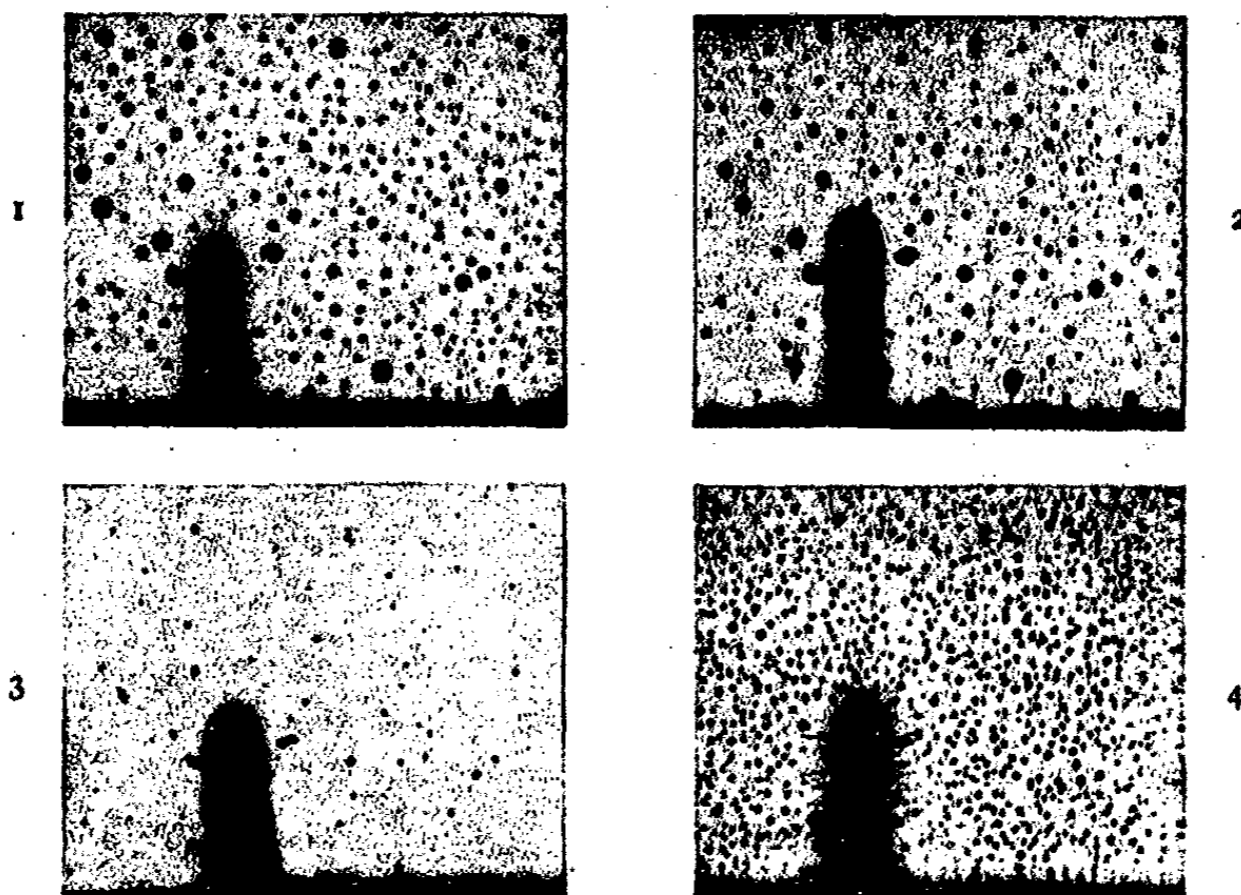
¹ Rebbeck and Ferguson: *J. Am. Chem. Soc.*, 46, 1991 (1924).

² Ferguson and Ellis: *Trans. Roy. Soc. Canada*, (3) 19, 34 (1925). (Abstract only.)

³ New glass signifies glass which has not been subjected to any especial treatment electrical, thermal or otherwise. The experimental procedure was similar to that used by Rebbeck and Ferguson.

first washed out with a dilute aqueous solution of sodium hydroxide and dried at 70°C by evacuation to 0.001 mm. mercury before trapping the hydrogen. Upon electrolysis under similar conditions for 72 hours, many of the bubbles disappeared and others became smaller. The experiments were carried out in duplicate and triplicate respectively.¹

A somewhat similar experiment with pure dry hydrogen was performed by trapping a small bubble in a well-annealed tube which was held in a horizontal



Plates 1-4

Gas Disappearance and Reappearance ($\times 100$).

Plate 1. A new soda-lime glass tube was electrolysed for 6.5 minutes at 95°C with 110 volts, mercury cathode.

Plate 2. The direction of the current was reversed and the electrolysis continued for 3.5 hours.

Plate 3. The previous electrolysis, mercury anode, was continued for 7.5 hours additional.

Plate 4. The mercury was made cathode and the tube electrolysed for 50 hours.

position, reducing the pressure until the bubble was several millimeters in diameter and then electrolysing with mercury anode at 150°C with 100 volts for 19 hours, at the same time slowly rotating the tube. The bubble did not appear to change. The pressure was increased to atmospheric and the electrolysis continued but with mercury cathode. No additional gas formed. When this experiment was repeated with hydrogen containing a little water vapour, on reversing the current, gas was produced in the form of a fine film which just covered the area traversed by the bubble during the rotation of the tube and did not extend beyond the edges of this area. This gas probably came from the reaction between the sodium from the glass and the sorbed

¹ The bubbles were identified by means of marks on the glass.

water since the hydrogen bubble did not progressively change in size during the electrolysis with mercury anode.

Cathode gas was previously observed with soda-lime glass and lead glass. It has since been obtained with Schott types 59^{III}, 16^{III}, 1447^{III}, 3818^{III}, 2814^{III}, 1003^{III} and Cavalier glass. A very long time elapsed before a visible film of gas was produced with the last mentioned glass and, in addition, those glasses which were heated in an oxy-gas flame in the preparation of the sample tubes required an exposure to moisture prior to the evacuation of the tubes and subsequent filling with mercury. Cathode gas, formed with 59^{III} and 16^{III}, disappeared in a normal fashion upon current reversal. Tests of this were not carried out with the other glasses.¹

If the initial formation of cathode gas on new soda-lime glass were the result of the action of sodium from the glass on the sorbed water, one would not expect to obtain gas with glass in which the sodium had been replaced with silver.² This conclusion was tested in the following manner. Silver was electrolysed into a new soda-lime glass tube from a melt of silver nitrate at 250°C using 110 volts for 7 minutes. The silver nitrate was removed; the tube was washed with nitric acid and distilled water, dried by evacuation and filled with mercury in the usual manner. It was electrolysed with mercury cathode at 100°C with 110 volt and no gas was visible after 60 minutes although a solid deposit formed at the interface which we assumed to be a mercury-silver compound. In a blank experiment, a tube containing no silver but subjected to the same heat treatment gave gas on subsequent electrolysis in 10 minutes and a similar tube through which sodium had been electrolysed at 330°C for 60 minutes from a sodium nitrate melt gave gas at the lower temperature in 17 minutes. However when silver was electrolysed into new soda-lime glass at 100°C from aqueous solution of silver nitrate, 0.02N, gas was produced using 110 volts at the same temperature.³

When well-annealed glass was substituted for new glass in the last experiment at 100°C, no gas was obtained but a solid deposit at the interface similar to that produced when a silver nitrate melt was initially employed, although the presence of moisture was indicated on a similar but unelectrolysed silver-containing tube upon treating it with sodium amalgam. The gas obtained in the experiment with new glass disappeared in a normal fashion on current reversal.

These experiments suggest that silver from an aqueous solution does not always uniformly replace the sodium in new glass although it may do so with annealed glass. The possible migration of hydrogen ions into glass was first

¹References for glass compositions: Pyrex, 59^{III}, 16^{III}, and Cavalier: International Critical Tables, Vol. II. Soda-lime glass, Redbeck and Ferguson: loc. cit. 1447^{III} and 397^{III}; Horovitz: Z. Physik, 15, 369 (1923). 3818^{III}: An informal communication from Schiller indicates the following composition: over 10%, Si and Na; under 10%, B, Al, Ca and K; traces, F and Mn.

²Schulze: Ann. Physik, 40, 335 (1913).

³Silver was first observed to enter glass from aqueous solutions by Mulligan: Trans. Roy. Soc. Canada, (3) 19, 35 (1925); also a note in a paper by Horovitz: Sitz. Akad. Wiss. Wien, 134 IIa, 383 (1925).

studied by Rebeck and Ferguson and their observations have more recently been supported by the work of Quittner.¹

Such migration may play some part in the phenomenon under discussion. The fact that gas formed on the new glass at 100°C when aqueous solutions of silver nitrate had previously been used, would disappear upon current reversal, points to the presence of sodium at the interface. This suggests that certain parts of the glass surface were impermeable to silver ions and that at these spots very little electrolysis took place, the potential gradient set up being only sufficient to form a very minute sodium-deficient layer. On current reversal, the sodium quickly reached the glass surface and reacted with the surface water. These spots would appear to be destroyed by annealing or by contact with a silver nitrate melt. The nature of them would seem to be bound up with the water content of the glass surface since both these treatments would tend to abstract the water. Also, Haber and Klemensiewicz² found that their glass electrodes behaved consistently as hydrogen electrodes only after they had steamed them for some hours. Horovitz after a careful study of the action of certain water-resistant glasses concluded that these acted as mixed electrodes and his work has been confirmed by others. Our observations although quite different in nature are in accord with his results.³

Rebeck and Ferguson found that 1.2 volts was above that required to just produce gas. The following factors prevent an exact determination of this voltage. Conditions may not be the same at all points on the glass surface. Some minutes are necessary for the building up of the counter E.M.F. and there may be a lapse of time between the formation of gas and the production of visible bubbles. Once electrolysis starts the various contact potentials in the system may all change and one cannot readily determine the nature of each. However, in one series of experiments gas was produced when the difference between the initial contact potential for the whole system and the applied voltage did not exceed 0.8 volts.

Since the sorption of water is involved in the disappearance of cathode gas, the question as to whether the current assisted in this was investigated. Gas was produced on a tube of new soda-lime glass at 100°C with 110 volts for 20 minutes and then caused to disappear by further electrolysis for many hours with mercury anode. A small amount of sodium amalgam was then added to the mercury in the tube and the latter held at 100°C without electrolysis for a time. After 30 minutes no gas was visible but after 20 hours a small amount could be seen under the microscope. The amalgam treatment also gave much less gas with new, or moistened annealed, soda-lime glass which had been electrolysed with mercury anode for long periods of time at 100°C with 110 volts, than with the new glass which was subjected to the same heat treatment alone prior to adding the amalgam. Since the amalgam reacts with such electrolysed tubes to give a dark deposit, there was the pos-

¹ Quittner: Sitz. Akad. Wiss. Wien, 136 IIa, 151 (1927).

² Haber and Klemensiewicz: Z. physik. Chem., 67, 385 (1909).

³ Horovitz: Z. Physik, 15, 369 (1923), and Sitz. Akad. Wiss. Wien, 134 IIa, 335 (1925).

sibility that there was not enough sodium for both reactions. This was not the case since the amalgam treatment gave gas and deposit on similar electrolysed tubes when these were moistened after electrolysis, dried by evacuation, refilled with mercury and then treated with amalgam. If after a small amount of gas was obtained with the electrolysed tubes using sodium amalgam, the tubes were then electrolysed with the amalgam as cathode more gas was obtained than in the case in which the tube with the amalgam had simply been given the same heat treatment. The results indicate that water may move into or out of glass under the influence of an electrical current. This may in part account for the slow reappearance of gas on current reversal after it has been caused to disappear but it is probably not the most important factor in this.

Anode Gas

Rebbeck and Ferguson obtained no anode gas at the mercury-glass interface at temperatures up to 100°C with 110 volts applied when the glass was properly cleaned. Le Blanc and Kerschbaum¹ did not observe any such gas even at 320°C but on subsequent heating of their samples to the softening point gas was liberated at the anode side. This gas nearly equalled the amount calculated by them from the sodium liberated at the cathode on the assumption that the anion SiO_3 had decomposed to give oxygen. The discrepancies between the calculated and observed amounts were attributed by them to their inability to remove all the oxygen from the viscous melts.

With soda-lime glass, anode gas has been produced using 110 volts at temperatures above 275°C . In one case, the gas formed on a freshly annealed tube at 310°C and later disappeared, giving rise to a dark deposit at the mercury-glass interface. This deposit clearly indicated the positions of the original bubbles. It was insoluble in water but dissolved in nitric acid. When smeared on the glass, it appeared to consist of red and yellowish materials and was similar in appearance to the deposits of mercury oxides which formed on the upper portions of tubes containing mercury when these were heated to a high temperature. Below 275°C small amounts of gas were obtained but we could not be sure if the minute amounts were true electrolytic products. However, deposits similar to those obtained at 310°C were observed at these lower temperatures. At 100°C traces were obtained using 110 volts and definite deposits were formed on a tube electrolysed over night at 100°C with 220 volts.

When a tube of soda-lime glass was electrolysed with 110 volts at 450°C for a long time using a carbon anode, the anode side of the glass was filled with bubbles some of which had broken the anode surface. The cathode surface of the glass was not visibly changed. On heating this glass it swelled and gave rise to the pumaceous product. In general our glass behaved like that of Le Blanc and Kerschbaum, but appeared to give gas at lower temperatures. These workers may have lost some gas through the oxidation

¹ Le Blanc and Kerschbaum: *Z. physik. Chem.*, 72, 468 (1910).

of the mercury and this may be an additional reason for their low results. The chief difference between their results and our own is the relatively low temperature at which anode gas was found by us to be liberated. This may be accounted for on the basis of glass composition since different glasses were used.

In conclusion we wish to thank Dr. Horovitz for the Schott glasses which he obtained for us.

Summary

1. New evidence has been submitted upon the formation and disappearance of cathode gas during the electrolysis of various glasses and on the permeability of glass to various ions.
2. Anode gas has been found to form at temperatures much lower than those previously reported.

*Toronto, Canada.
October, 1927.*

SOME PHYSICAL PROPERTIES OF AQUEOUS HYDROXYBENZENE SOLUTIONS

BY LLOYD E. SWEARINGEN

The mono, di- and tri-hydroxybenzenes form a class of substances important and peculiar unto themselves. The mono derivatives, as well as some of the di and tri derivatives are common substances met with in a number of widely different preparations and uses. In spite of their somewhat wide-spread usage, little work has been done on the physical properties of aqueous solutions of this class of substances. This is especially true of the di- and tri-hydroxy derivatives. Their solubility in water is known; the water-phenol system has been exhaustively studied; Skraup and Philippi¹ have studied the capillary rise of phenol-water solutions; Thiel and Roemer² have studied the acid properties of the phenols by electric titration methods. Morgan and Egloff³ have measured the surface tension of phenol-water mixtures by the drop weight method. Worley⁴ has measured the surface tension of phenol-water mixtures by the capillary rise method. More recently, Ferguson⁵ has determined the specific heats, the heats of mixing and the vapor pressures of mixtures of phenol and water.

In view of the small amount of physical data available for solutions of this class, the following measurements have been carried out with the view of contributing something to the knowledge of properties of this class of solutions. The surface tension, the density, the index of refraction and the viscosity of these solutions have been determined.

Experimental

Material

Water. The water used in these experiments was a good grade of conductivity water, twice distilled from acid permanganate and barium hydroxide, then collected and stored in well steamed and cleaned pyrex glassware.

Phenol. Merck and Company. "Absolute Phenol." C.P.

Catechol. E. & A. Resublimed. M.P. 103-104°C.

Resorcinol. Mallinckrodt. C.P. quality. Free from di-resorcin, phenol and acid. M.P. 108-100°C.

Hydroquinol. Merck and Company. Highest Purity.

Pyrogallol. Merck and Company. M.P. 128-131°C.

Phloroglucinol. Merck and Company. Extra Pure. Free from di-resorcin.

* Contribution from the Chemical Laboratory of the University of Oklahoma.

¹ Monatsheft, 32, 353-72 (1911).

² Z. physik. Chem., 63, 711-61 (1908).

³ J. Am. Chem. Soc., 38, 844 (1916).

⁴ J. Chem. Soc., 105, 260 (1914).

⁵ J. Phys. Chem., 31, 757 (1927).

Procedure

A quantity of each of the above hydroxybenzenes, sufficient to make 200 c.c. of a 0.5 molar solution was accurately weighed out and then dissolved in the required amount of water. In the case of phloroglucinol, due to the small sample available, the solution prepared was only 0.0836 molar.

The surface tensions, densities, indices of refraction and the viscosities of the original solutions were determined. Then a definite quantity of each of the solutions was mixed with water in such proportion as to decrease the con-

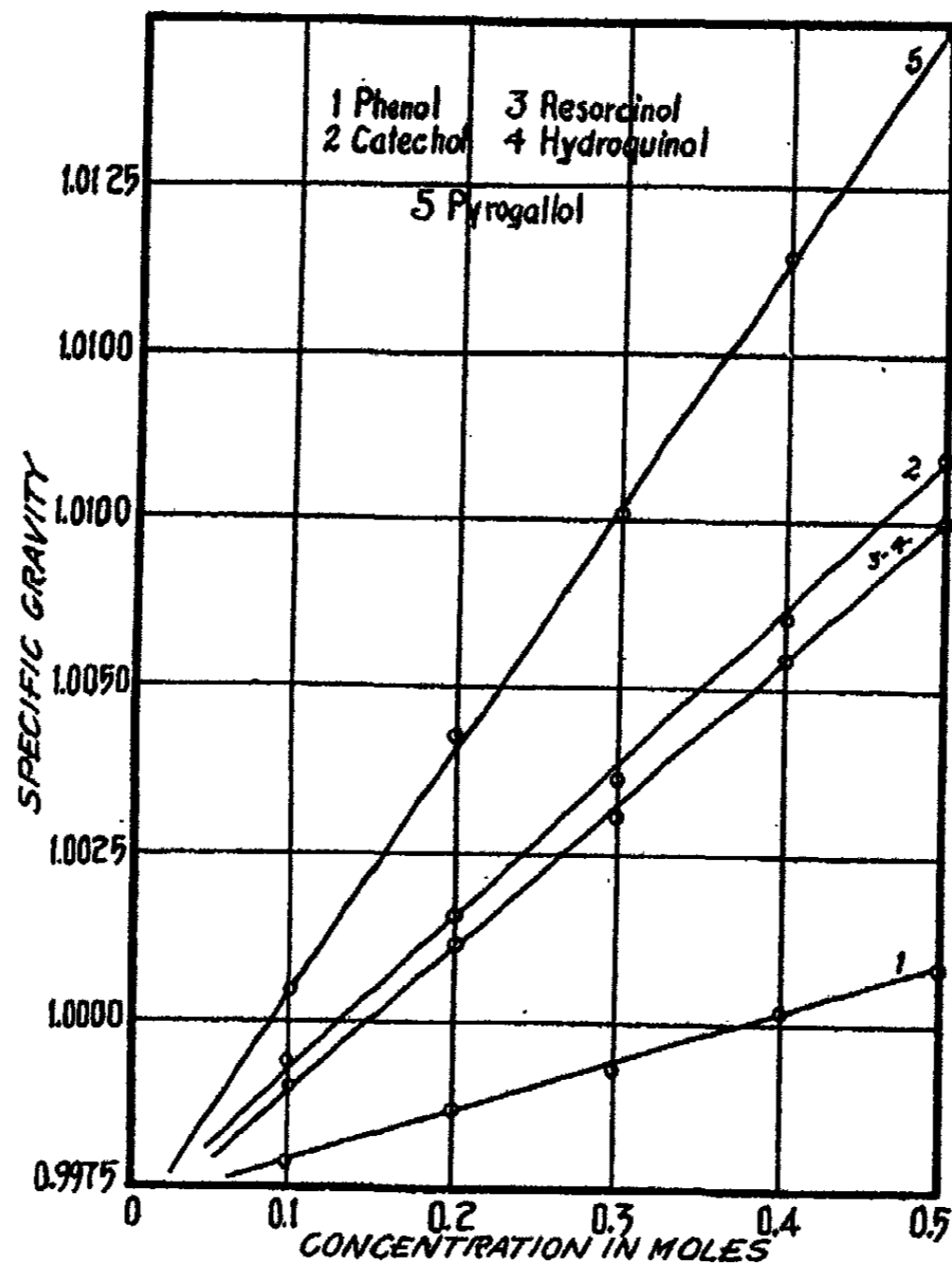


FIG. 1

centration of the solute to 0.8, 0.6, 0.4, 0.2 of the original value, so that in this way a series of solutions of 0.5, 0.4, 0.3, 0.2 and 0.1 molar concentration was prepared for each of the hydroxybenzenes. The physical properties were then determined for each of the different solutions.

Density

The density of the different solutions was determined by the pycnometer method, using a Geissler pycnometer. The measurements were made at 25°C. and the value of $D_{4}^{25^{\circ}\text{C}}$ calculated. Table I gives a summary of the density

determinations. The values given are the averages of three determinations. The separate determinations differed by less than .05% from each other. Correction has been made for the buoyancy of the air. The variation in specific gravity with density is shown graphically in Fig. 1.

Viscosity

The viscosity measurements were taken at 25°C with a modification of the Ostwald-Poiseuille viscometer. The temperature could be controlled to within 0.1°C. The time of outflow was measured with a stop watch, reading direct

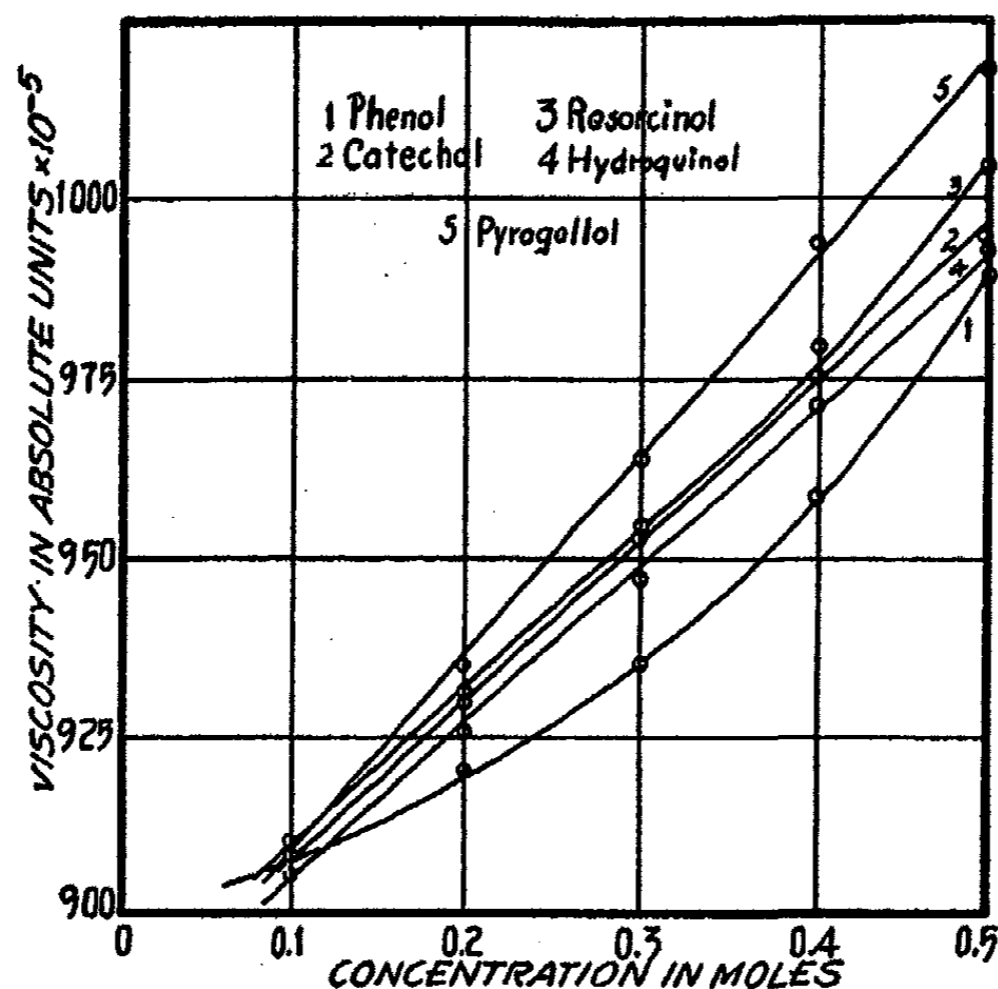


FIG. 2

to 0.2 second. The usual precautions were taken in cleaning, washing and drying the tube. The viscosity measurements are given in Table II. The data given are averages of three separate determinations. The time for each determination within a series was reproducible to within 0.4 sec. For all solutions more than 100 sec. was required for outflow. For conversion to absolute units, the value (0.00894 c.g.s. units) of Bingham and Jackson¹ was used. The effect of concentration on the viscosity is shown graphically in Fig. 2.

Index of Refraction

The index of refraction was measured at 25°C with an Abbe refractometer. The temperature was constant at 25°C to 0.1°. The indices of refraction are given in Table III. The readings given are averages of four separate readings. The variation of the index of refraction with density is shown in Fig. 3.

¹Bull. Bur. Standards, 14, (1), 59 (1918.)

TABLE I

The Density of Aqueous Hydroxybenzene Solutions

| Concentration in moles/liter | D ^{25°C} _{25°C} | D ^{25°C} _{4°C} | Concentration in moles/liter | D ^{25°C} _{25°C} | D ^{25°C} _{4°C} |
|---------------------------------|-----------------------------------|----------------------------------|---------------------------------|-----------------------------------|----------------------------------|
| Phenol | | | Hydroquinol | | |
| 0.5 | 1.0039 | 1.0009 | 0.5 | 1.0106 | 1.0076 |
| 0.4 | 1.0032 | 1.0002 | 0.4 | 1.0086 | 1.0056 |
| 0.3 | 1.0023 | 0.9993 | 0.3 | 1.0061 | 1.0031 |
| 0.2 | 1.0017 | 0.9987 | 0.2 | 1.0042 | 1.0012 |
| 0.1 | 1.0008 | 0.9978 | 0.1 | 1.0024 | 0.9994 |
| Phenol | | | Pyrogallol | | |
| 0.5 | 1.0115 | 1.0085 | 0.5 | 1.0180 | 1.0149 |
| 0.4 | 1.0091 | 1.0061 | 0.4 | 1.0145 | 1.0115 |
| 0.3 | 1.0066 | 1.0036 | 0.3 | 1.0106 | 1.0076 |
| 0.2 | 1.0046 | 1.0016 | 0.2 | 1.0073 | 1.0043 |
| 0.1 | 1.0024 | 0.9994 | 0.1 | 1.0035 | 1.0005 |
| Resorcinol | | | Resorcinol | | |
| 0.5 | 1.1015 | 1.0075 | 0.2 | 1.0042 | 1.0012 |
| 0.4 | 1.0085 | 1.0055 | 0.1 | 1.0021 | 0.9991 |
| 0.3 | 1.0061 | 1.0031 | | | |

TABLE II

Relative and Absolute Viscosities of Aqueous Hydroxybenzene Solutions. 25°C

| Concentration moles/liter | Relative Viscosity | Absolute Viscosity | Concentration moles/liter | Relative Viscosity | Absolute Viscosity |
|------------------------------|-----------------------|-----------------------|------------------------------|-----------------------|-----------------------|
| Phenol | | | Hydroquinol | | |
| 0.5 | 1.1062 | 0.00989 | 0.5 | 1.1106 | 0.00993 |
| 0.4 | 1.0774 | 0.00959 | 0.4 | 1.0873 | 0.00972 |
| 0.3 | 1.0480 | 0.00935 | 0.3 | 1.0655 | 0.00953 |
| 0.2 | 1.0287 | 0.00920 | 0.2 | 1.0353 | 0.00926 |
| 0.1 | 1.0158 | 0.00908 | 0.1 | 1.0134 | 0.00906 |
| Catachol | | | Pyrogallol | | |
| 0.5 | 1.1126 | 0.00995 | 0.5 | 1.1391 | 0.01018 |
| 0.4 | 1.0960 | 0.00976 | 0.4 | 1.1119 | 0.00994 |
| 0.3 | 1.0660 | 0.00953 | 0.3 | 1.0783 | 0.00964 |
| 0.2 | 1.0398 | 0.00930 | 0.2 | 1.0456 | 0.00935 |
| 0.1 | 1.0184 | 0.00910 | 0.1 | 1.0186 | 0.00911 |
| Resorcinol | | | Resorcinol | | |
| 0.5 | 1.1247 | 0.01005 | 0.2 | 1.0414 | 0.00931 |
| 0.4 | 1.0952 | 0.00979 | 0.1 | 1.0191 | 0.00911 |
| 0.3 | 1.0580 | 0.00947 | | | |

TABLE III

The Index of Refraction of Aqueous Hydroxybenzene Solutions. 25°C

| Concentration moles/liter | Index of Refraction | Concentration moles/liter | Index of Refraction |
|------------------------------|------------------------|------------------------------|------------------------|
| Phenol | | Hydroquinol | |
| 0.5 | 1.3419 | 0.5 | 1.3422 |
| 0.4 | 1.3386 | 0.4 | 1.3398 |
| 0.3 | 1.3368 | 0.3 | 1.3373 |
| 0.2 | 1.3353 | 0.2 | 1.3363 |
| 0.1 | 1.3343 | 0.1 | 1.3352 |
| Catechol | | Pyrogallol | |
| 0.5 | 1.3436 | 0.5 | 1.3437 |
| 0.4 | 1.3397 | 0.4 | 1.3414 |
| 0.3 | 1.3373 | 0.3 | 1.3388 |
| 0.2 | 1.3369 | 0.2 | 1.3370 |
| 0.1 | 1.3348 | 0.1 | 1.3345 |
| Resorcinol | | Resorcinol | |
| 0.5 | 1.3443 | 0.2 | 1.3366 |
| 0.4 | 1.3405 | 0.1 | 1.3353 |
| 0.3 | 1.3385 | | |

TABLE IV

The Surface Tension of Aqueous Hydroxybenzene Solutions. 25°C

| Concentration moles/liter | DialReading Units | SurfaceTension Dynes/cm. | Concentration moles/liter | DialReading Units | SurfaceTension Dynes/cm. |
|------------------------------|----------------------|-----------------------------|------------------------------|----------------------|-----------------------------|
| Phenol | | | Hydroquinol | | |
| 0.5 | 77.5 | 49.1 | 0.5 | 112.7 | 71.4 |
| 0.4 | 82.7 | 52.5 | 0.4 | 113.25 | 71.8 |
| 0.3 | 87.35 | 55.3 | 0.3 | 114.50 | 72.5 |
| 0.2 | 94.10 | 59.6 | 0.2 | 115.40 | 73.2 |
| 0.1 | 103.90 | 65.8 | 0.1 | 116.20 | 73.7 |
| Catechol | | | Pyrogallol | | |
| 0.5 | 100.80 | 64.0 | 0.5 | 113.30 | 71.8 |
| 0.4 | 101.59 | 65.1 | 0.4 | 114.75 | 72.60 |
| 0.3 | 105.15 | 66.70 | 0.3 | 115.50 | 73.15 |
| 0.2 | 108.20 | 68.50 | 0.2 | 116.1 | 73.60 |
| 0.1 | 112.50 | 71.3 | 0.1 | 117.00 | 74.1 |
| Resorcinol | | | Resorcinol | | |
| 0.5 | 109.1 | 69.1 | 0.2 | 113.15 | 71.7 |
| 0.4 | 110.5 | 70.0 | 0.1 | 115.65 | 73.2 |
| 0.3 | 111.6 | 70.6 | | | |

Surface Tension

The surface tension measurements were made with a du Notty Tensiometer. The instrument was calibrated with water at 25°C, a value of 74.46 dynes/cm being obtained for water at 25°C. 5 c.c. portions of the different solutions were placed in deep watch glasses and the glasses placed in a water bath at 25°C. The watch glasses were carefully cleaned and flamed before use. The readings given are the averages of six determinations. These readings were reproducible within 0.1 scale unit. The measurements are shown in Table IV and Fig. 4.

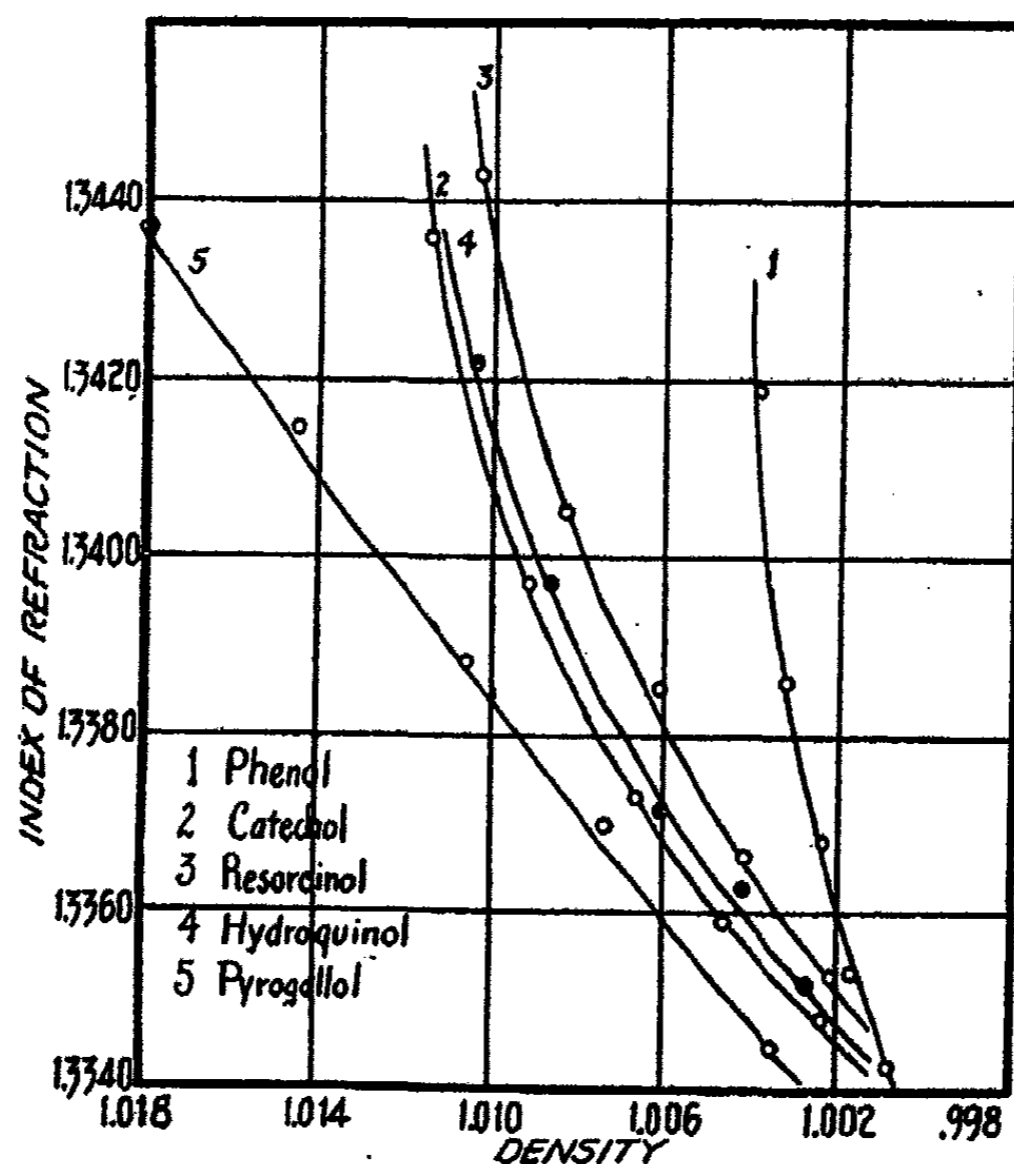


FIG. 3

Discussion

No irregularity is apparent in the data for the density of the solutions. Two of the three di-hydroxy derivatives, the meta (1:3) and the para (1:4) have almost identical densities, while that of the ortho (1:2) is but slightly greater at corresponding concentrations. Reference to Fig. 1 shows an almost linear relation between concentration and specific gravity. The densities of the different solutions can be calculated very accurately from the law of mixtures. If the equation for a straight line be written as $D = mC + D_0$, the densities can be calculated very accurately. D is the density to be found, m a

constant, characteristic for each substance, C the concentration in moles/liter and D_0 the value for the average density of the solution at zero concentration of solute. m is the value of dD/dC , the change in density with concentration. The values of m for the different hydrobenzene solutions are as follows:

| | m | | m |
|------------|--------|-------------|--------|
| Phenol | 0.0075 | Hydroquinol | 0.0210 |
| Catechol | 0.0230 | Pyrogallol | 0.0350 |
| Resorcinol | 0.0210 | | |

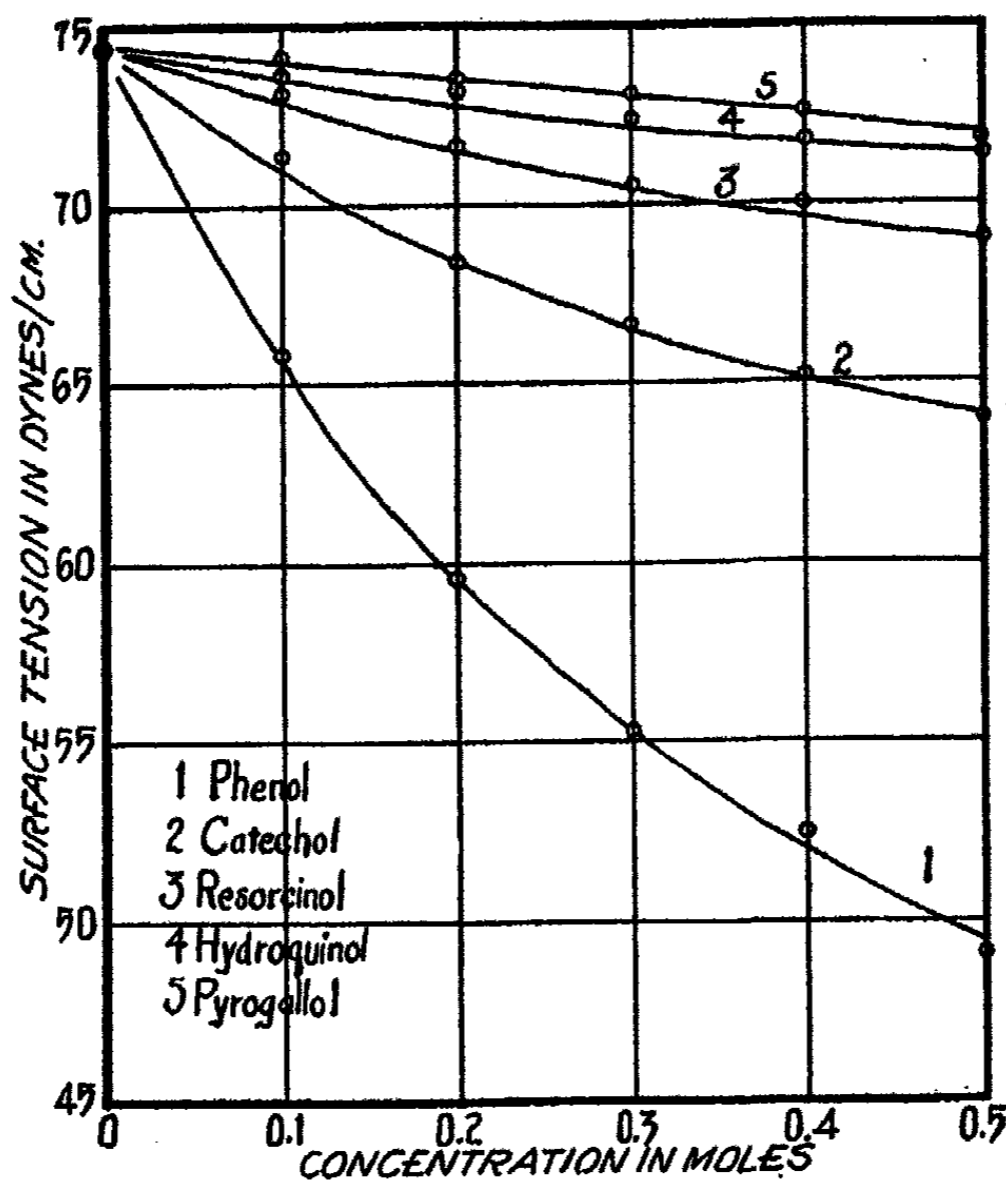


FIG. 4
Surface Tension—Concentration Curves

An increase in the number of hydroxy groups in the benzene ring seems to produce an exaltation in the viscosity, as for all concentrations investigated, there is an increase in viscosity in going from the mono- thru the di- to the tri-hydroxy derivatives. The position of the hydroxyl group seems to have but little influence, as all of the di-hydroxy derivatives possess viscosities very nearly the same, the meta having a slightly higher viscosity than the ortho, which in turn has a viscosity slightly greater than the para derivative. The introduction of the third hydroxyl group tends to cause a considerable increase in the viscosity at all concentrations except the lowest, where all the viscosities are but slightly different from that of pure water. Viscosity con-

centration curves of the type shown in Fig. 2 are similar in character to those of approximately normal substances, showing little or no association or dissociation in water.

The index of refraction exhibits but little change with changes in density or concentration. The change is greatest with phenol, less with the di-hydroxy derivatives and still less with the trihydroxy derivative. The three di-hydroxy derivatives show but slight variation among themselves.

The surface tension values of the phenols in water determined by Skraup and Philippi are not available, but the order of decreasing rise given by these workers is as follows: Phenol, catechol and hydroquinol rise to about the same height. Resorcinol and pyrogallol give lower values in the order named. This order is the same as found in the present work, with the exception of the position of hydroquinol and resorcinol. The values of the surface tension of phenol and water in the present work are slightly greater than those reported by Morgan or Worley.

The surface tension values show considerable variation depending on the number and position of the hydroxyl groups. Each molecule of phenol is much more effective in lowering the surface tension of water than is a molecule of the di- or tri-hydroxybenzene. The di-hydroxybenzenes stand in the order, ortho, meta and para, in their ability to lower the surface tension of water. This order is the same as their order of increasing melting points. The highest melting point compound lowering the surface tension less than those of lower melting point. Pyrogallol lowers the surface tension of water but slightly. The melting point of pyrogallol is between the melting points of the meta and para di-hydroxy derivative.

As we go from benzene, which is but slightly soluble in water to phenol which is moderately soluble at room temperature, to the di- and tri-hydroxy derivatives, the enhanced solubility of these latter is usually ascribed to an increase in the number of hydroxyl groups in the benzene ring. The fact that water is a polar substance and the polar properties of the hydroxyl group have long been recognized.

Surface tensions of a series of similar substances will usually follow the same general order as the melting points, if solids, or the boiling points, if liquids. Other factors being the same, a molecule of phenol should be more effective in lowering the surface tension of water than a molecule of the di- or the tri-hydroxy derivative, due to the lower surface tension of the phenol. Fewer phenol molecules than di- or tri-hydroxybenzene molecules would need be concentrated in the surface to produce a given lowering in the surface tension of water.

0.02 mole of phenol produces as great a lowering in the surface tension of water as 25 times that much pyrogallol; as 20 times the para, 8.5 times the meta and 3.5 times the ortho di-hydroxy benzenes. Undoubtedly more of the highly capillary active phenol molecules are in the surface layer than are the di- and tri-hydroxy molecules at corresponding concentrations. Otherwise, it would be difficult to account for the appreciable lowering of the surface tension of water by phenol. The di- and tri-hydroxybenzenes undoubtedly

have higher surface tension values than phenol and are incapable of lowering the surface tension of water to such a degree as phenol. But in view of the high concentration of the di- and tri-hydroxy derivatives required to produce a lowering corresponding to a small concentration of phenol, it is logical to assume a much smaller surface concentration of the di- and tri-derivatives than of phenol.

Evidently, the increased number of hydroxyl groups encountered in going from the mono to the tri derivatives produces a greater resemblance between the hydroxybenzene molecules and water, with the result that the di- and the tri-hydroxybenzene molecules concentrate less readily in the surface and more readily in the bulk of the solution.

Summary

1. The density, viscosity, index of refraction, and surface tension of aqueous solutions of hydrobenzenes have been determined at 25°C.
2. No pronounced effect due to the number or position of the hydroxyl groups has been found except in the case of surface tension.
3. The monohydric derivative is more effective than the dihydric derivative, which in turn is more effective than the trihydric derivative in lowering the surface tension of water.

Norman, Oklahoma.

NEW BOOKS

Physical Chemistry and Biophysics for Students of Biology and Medicine. By Matthew Steel. 23 × 15 cm; pp. x + 372. New York: John Wiley and Sons, 1928. Price: \$4.00. The subject is treated under the following headings: general introduction; the nature and structure of matter; general properties of matter; energy transformations in living matter; general nature of solutions; water, the greatest solvent; diffusion and osmotic pressure; the nature and behavior of electrolytes in solution; chemical equilibrium and the law of mass action; measurement of hydrogen ion concentration; the colloidal state of matter; catalysis and velocity of chemical reactions; dynamical physical chemistry of the cell.

This book is apparently written for use in an undergraduate medical school because the author says that "the treatment of the subject is based on the course in physical chemistry pursued by medical students at the Long Island College Hospital." Under these circumstances the book should have been kept as simple and as accurate as possible.

Instead of this the author says that "considerable attention is given to the modern conception of the nature and structure of matter because the composition of the atom is the keynote of the properties of matter in all the various states of aggregation. Without a knowledge of the present-day theories in regard to the nature and structure of the atom, it is impossible for the student to comprehend such topics as the cause of ionization, the nature of amphoteric electrolytes and their isoelectric points, hydrogen-ion concentration, Donnan's membrane equilibria theory, oxidation-reduction phenomena in the absence of free oxygen or hydrogen," p. v.

Hydrogen ion concentrations and amphoteric electrolytes were studied before anything was known about the composition of the atom. We can only marvel at the wonderful ingenuity of Donnan in deducing a relation which, by definition, he could not comprehend.

The author got much of his physical chemistry from H. C. Jones and he says that "in the chapter on the Colloidal State of Matter the researches of Jacques Loeb on proteins have received special attention owing to the far-reaching influence that Loeb's discoveries and conclusions have on all biological and medical problems." Even that does not account for all the characteristics of the book. The author must have thought of some things himself.

On p. 12 is the statement that "one of the types [of sulphur] crystallizes in rhombic crystals and the other in monoclinic crystals. Both have the same freezing-point and boiling-point." They don't have the same freezing-point and crystals don't have boiling-points.

There is no definite policy in regard to people. On p. 23 we read that "at the suggestion of Becquerel, Mme. Curie (Marie Sklodowska Curie), Professor of Physics at the Sorbonne, Paris, studied uranium minerals." The author means of course that Mme. Curie is now Professor of Physics. That is legitimate enough; but what is the student going to do when he reads, on p. 24, that "the first noteworthy evidence in regard to the true character of the radiations was presented by Sir Ernest Rutherford, Professor of Physics at the University of Manchester." Rutherford is certainly not at Manchester now.

On p. 62 is the statement that "chemists have decided to adopt eight grams of oxygen as the standard of comparison." On p. 65 is the paragraph that "matter occurs in different states or conditions known as *states of aggregation*. The three principal states of aggregation the *gaseous state*, the *liquid state*, and the *crystalline state*. There is another important modification of the latter two states, known as the *colloidal state*. In addition there are *amorphous solids*, *solid liquids*, and *liquid crystals*." That is helpful to the student.

It would take a good man to deduce, p. 67, the equation

$$pv = p_0v_0(1 + 0.00367 t)$$

from the preceding two equations on the same page. It is just possible that the author did not know the intermediate steps and therefore skipped them. The reviewer could not discover the difference between v and V , p. 68. Nobody would guess, p. 71, that a and b in the

van der Waals equation are not really constants. The statement of Berthelot's law on p. 87 is a bit sweeping for a heading of general concept of energy. It might also be questioned whether "we owe much of our knowledge of chemical energy to the French chemist, Berthelot."

"With regard to the influence of the nature of the gas on the solubility, it may be said in general that the extremely soluble gases, like ammonia and hydrogen chloride, do not obey Henry's law in the matter of solubility, i.e., their solubility is not proportional to the pressure. This is undoubtedly due to their distinct basic and acidic properties which induce them to form compounds with the solvent. Thus, NH_3 unites with H_2O to form NH_4OH , and HCl unites with H_2O to form a hydrate, $\text{HCl}\cdot\text{H}_2\text{O}$," p. 108. It is not impossible that hydrochloric acid forms a hydrate, $\text{HCl}\cdot\text{H}_2\text{O}$; but that is not the chief reason for hydrochloric acid not following Henry's law.

Under solutions of liquids in solids, p. 113, the author says that "solids also have the property of taking up many liquids in greater or less quantities. Many of the substances that we are accustomed to think of as solids are really mixtures of solids and water. Moreover, it is very difficult to obtain these solids free from water." One man's guess is as good as another's as to what the author is talking about."

On p. 116 no one would ever guess that the order of dissociating power of liquids does not always run parallel with the dielectric constant.

"Solutions of the second class, those whose osmotic pressure is greater than the values obtained in the first class, include the acids, bases, and salts, i.e., those substances that conduct electricity when dissolved in water, and some other solvents. Now, as these constitute a very large and important class of compounds, their failure to conform to the laws that apply to the first class prevented the general acceptance of van't Hoff's theory of solutions for a long time," p. 132. Since very few people read academy publications, the long time to which the author refers was a few days over two months.

On p. 134 is the statement that "there are several other theories of semipermeable membranes which have many data to back them up, but they are not as plausible as the *preferential solubility* theory." Regardless of what the reviewer may have said in the past, he is quite sure now that the copper ferrocyanide membrane does not owe its properties to preferential solubility. Without looking the matter up, the reviewer doubts whether Soret explained his phenomenon by establishing the relationship between diffusion and osmotic pressure, p. 144. It is usually believed that van't Hoff explained the Soret phenomenon.

On page 163 we read that "both the ampere and the volt are based upon another law as fundamental as Ohm's law, discovered by Faraday in 1833"; but we are not told what Faraday's law has to do with the volt. On p. 206 the author takes a running leap into the unknown and says that "the solution pressure of a metal remains constant so that any change in potential is due entirely to a change in osmotic pressure." He evidently believes that there is a definite relation between the calculated pH and the hydrogen ion concentration. On p. 210 he says that "if, for example, $C_1 = 1$ gram-equivalent of H^+ ion per liter, and if we represent C_2 by H^+ , we can obtain the value of the unknown hydrogen-ion concentration by means of the equation $E = 0.058 \log_{10} (1/\text{H}^+)$ ". This is undoubtedly true; but there is nothing to show what solution contains exactly one gram-equivalent of hydrogen ion per liter. Even if the author knew one, how would he get anybody else to agree with him and does the equation hold for normal solutions? Are we justified in saying, p. 212, that "under normal conditions a potential of +0.56 volts is developed in the calomel electrode?"

Under "Preparation of Colloidal Solutions," p. 231, there is nothing to show under what conditions or why a colloidal solution is formed. It is not true, as the author implies, p. 233, that one can remove the peptizing agent from a sol by dialysis and still have a sol. It is possible to remove some of it; but when you take away the last straw, the horse dies.

"When emulsoids are added to suspensoid sols the general reaction is that described under the caption of "protective colloids." Some precipitation may take place if they are oppositely charged, but the reaction is never complete, and as rule the suspensoid acquires the charge of the emulsoid owing to the coating effect. No generalizations have been established," p. 265. The author could have done better than this.

On p. 280 is the extraordinary statement that "emulsions are of two kinds: (1) a small quantity of a liquid in suspension in a large amount of another liquid; and (2) a large amount of one liquid suspended in another liquid. In the second class the continuous phase must consist of a solution of a colloid, such as soap, protein, or saponin." The author has heard of oil-in-water and of water-in-oil emulsions because he refers to them later, p. 356. What he is trying to do here, though unsuccessfully, is to differentiate between an emulsion stabilized by an adsorbed ion and one stabilized by an adsorbed substance.

The reviewer is sceptical about the statement, p. 284, that "the effect of heat on a gelatin sol is very different from its effect on a protein sol. Both gelatin and agar dissolve in hot water. The solution on cooling sets to a jelly. If a rather concentrated gelatin sol is heated and then permitted to cool, the jelly is not reconverted into a sol when the temperature is raised again, unless more water is added."

The reasoning about proteins is beautifully simple, p. 284. There are some free amino and carboxyl groups in the proteins and consequently they must form salts. Since they form salts there must have been some free amino and carboxyl groups. The treatment of the Hofmeister series, p. 290, is almost equally good. Loeb worked under conditions of dilution for which only the adsorption of hydrogen and hydroxyl ions was important and drew the conclusion that the Hofmeister series was meaningless. Other people worked under more intelligent conditions and found the Hofmeister series. The author points out triumphantly that these people do not, however, deny the validity of Loeb's work. What they denied and still deny is the validity of Loeb's conclusions. Procter, p. 298, "assumed a gelatin sol to contain gelatin ions which cannot diffuse into the surrounding water through the surface of the gelatin." We are not told why gelatin ions should not form on the outside.

The author is unnecessarily vague about jellies, p. 306. He says that most authorities consider a jelly as a two-phase system in which the dispersing agent is a solid and the dispersed phase a liquid. Four lines later he says that a concentrated gelatin jelly consists of "a solid phase, rich in gelatin, which forms a meshwork in the interstices of which is imbedded a very much more liquid second phase." If we have a mesh-work, we cannot speak of a dispersing and a dispersed phase, because each phase is continuous. It is what the reviewer has called an interlacing system. The author would hardly say that air is dispersed in a coil of wire fence no matter how small the meshes were.

There are good passages in the book. The reviewer found two that interested him particularly. "The red blood corpuscles are an easy cell to work with, on account of the ease with which they can be obtained. The contents of these cells is enclosed in a thin elastic envelope, but, unlike the plant cells, they have no resistant cell wall to support the membrane; consequently, when they are placed in water they readily swell up and finally burst, thereby liberating the coloring matter of the cell, the haemoglobin, so that the water acquires a deep-red color. This is called laking," p. 137.

"Van Slyke, while studying acidosis, made a very careful study of the pH of blood, and found that the maximum normal range of variation of reaction in different individuals is indicated by pH 7.30-7.50. Under extreme abnormal conditions the pH may fall slightly below 7.0, or may rise as high as 7.8. With the former condition *coma* occurs, while with the latter *tetany* is generally present," p. 327.

The reviewer was also interested in the paragraph on the poisonous action of pure water, p. 148, though he does not feel sure that the harmful action of eating snow or ice is entirely an osmotic pressure phenomenon. There might be a temperature effect. It also seems probable to the reviewer that the author has over-emphasized the dangers of drinking distilled water.

Wilder D. Bancroft

Crystalline Form and Chemical Constitution. By A. E. H. Tutton. 23 × 15 cm; pp. xii + 262. London: Macmillan and Co., 1926. Price: \$3.80. The subject is treated under the general headings: introduction; the main facts of crystallography; isomorphism; improved methods of crystallographic research; the research on the alkali sulphates and selenates; the research on the hexahydrated double sulphates and selenates; general con-

clusions regarding isomorphism; parallel growths, overgrowths, and mixed crystals; isogonism, polymorphism, and polysymmetry; enantiomorphism and optical activity—quartz as a typical example; enantiomorphism and optical activity—tartaric acid as example; remarkable cases and conclusions concerning optical activity; liquid crystals; Fedorov's crystallochemical analysis; general conclusions.

The reviewer was much interested in the view recorded on p. 29, which differs considerably from the popular one. "In the simpler cases, such as those of binary compounds like the chlorides of sodium and potassium, NaCl and KCl, or those containing only three elements such as calcite, CaCO_3 , the arrangement of the atoms of the different chemical elements is directly given by the X-ray results, and the structure thus appears as if it were of atoms and not of molecules, although of course the molecules are really there, as they were deposited from the saturated solution as such. These simpler cases have become referred to, probably not very accurately or advisedly, as 'ionised crystal-structures.' Yet in the face-centred cube of either rock-salt or potassium chloride, and in the corresponding face-centred rhomb of calcite, four chemical molecules definitely go to compose this unit-cell of the space-lattice. But in the case of complicated compounds, such as those of organic substances like tartaric acid or naphthalene, what is directly revealed is the molecular arrangement, that of the space-lattice, the unit-cells of which are composed of one to four molecules; in the cases of both tartaric acid and naphthalene there are two chemical molecules, $\text{C}_4\text{H}_6\text{O}_6$ and C_{10}H_8 respectively, to each cell. The chemical molecule in these cases is very definitely present, and the exact way in which the two are arranged with respect to each other has been determined. Now as the molecule goes into the crystal with practically no change, the stereometric arrangement of its atoms, and its consequent chemical constitution, is a matter of immense importance, and if the arrangement of the atoms shows any elements of symmetry these must have an influence on, and indeed take part in, the crystal symmetry, and assist in determining the particular class of the system which is developed."

"The original principle, formulated by 'the father of crystallography,' the Abbé Haüy, in the year 1782, was that 'every single substance, definitely chemically constituted, possesses its own crystalline form.' This was intended further to mean that "the angles between the faces of this form are peculiar and special to the substance." We must add to this, from later knowledge, 'unless it be of cubic symmetry.' For the perfect symmetry of the cubic system itself determines the angles of the cubic forms, which are, therefore, invariable. We can also truthfully add, which substantiates Haüy even for cubic substances, 'and, whatever the symmetry, even if cubic, is endowed with its own crystallographic physical properties, such as crystal density, optical refraction, elasticity, and electrical constants.'

"The facts above stated between inverted commas are now established without fear of contradiction. Even if the substance be polymorphous, the two or more forms are unlike that or those of any other body," p. 5.

In 1812 Wollaston showed that the angles of such similar forms as calcite, siderite, and dolomite "were not identical, but differed quite appreciably, well beyond the possible experimental error of his [newly invented] goniometer. For instance, he gave for the rhombohedral angle of calcite $105^\circ 5'$, for that of dolomite $106^\circ 15'$, and that of chalybite $107^\circ 0'$, precisely the values accepted today after repeated remeasurement by several later crystallographers," p. 36.

"There can be no question whatever that to Wollaston belongs the credit of having not only discovered isomorphism, but of showing that outside the cubic system isomorphous substances possess their own exact form, with angles distinct from those of every other substance, even those of the same isomorphous series. It is high time that this credit were assigned to him," p. 37.

"Quite apart from the question of the strict interpretation of the term isomorphism, a result of immense importance to chemistry at once sprang from the magnificent work of Wollaston and Mitscherlich, largely owing to the fact that Berzelius, who was so interested in Mitscherlich, was the greatest living authority on the equivalents and atomic weights

of the elements. It was obvious that the substances which were shown to be isomorphous were chemically analogous, and it was usually the case that an isomorphous group was formed by the interchange of elements belonging to the same family group, or acting chemically similarly, that is, the different members of the isomorphous series were of similar chemical constitution, and only differed in having present in each case a different member of a family group of closely allied and similarly behaving chemical elements. Thus in the sulphate-selenate series, selenium, which is an element of the sulphur group, having similar combining power (valency) and forming the same type of compounds, replaces sulphur without immediately apparent change of crystal form. Now Berzelius, in studying the chemical relationships of all the elements known up to that time, had found great difficulty in fixing the atomic weights from the equivalents, and thereby defining their positions among the elements, of quite a number of elements, and not only indeed the rarer and more lately discovered ones. But here in the principle of isomorphism was a new ally, and most of these difficult cases were at once cleared up by the application of the new principle, the salts of these elements being found to be isomorphous with those of well-understood elements about whose positions there was no ambiguity. The elements which he thus correctly placed in position, and the atomic weights of which he was able to fix, were copper, cadmium, zinc, nickel, cobalt, iron, manganese, chromium, sulphur, selenium, and chlorine. Also the queer case of the ammonium salts, in which the base ammonium was known to replace potassium isomorphously, was eventually settled. For at this time the constitution and composition of ammonium was a matter of bitter controversy. It was finally shown that it was ammonia gas, nitrogen hydride, NH_3 , with an additional atom of hydrogen, namely, NH_4 , that acted as a radicle or group-entity in replacing an atom of potassium," p. 41.

"Specific chemical substitutions invoke localised changes in the crystal structure, one crystal-axial direction frequently suffering much more change than the others, indicating that the chemical atoms occupy definitely localised positions in the crystal unit, the space-lattice cell, and therefore in the crystal molecule (the chemical molecule as it exists in the solid crystal state) or molecules (four in the rhombic series of sulphates and selenates, confirmed by X-ray analysis, and probably two at most, and possibly only one, in the double salt series) which compose the 'cell.' The actual positions of the atoms thus definitely fixed have, long after this fact was first published by the author, since been revealed by means of X-rays, which, by reason of their wave-lengths being of the same order of dimensions as the atoms, are capable of reflection from or diffraction by the space-lattice-planes of atoms, at definite glancing angles for X-rays of specific ("monochromatic") wave-length, which enable the spacing of the planes to be calculated in absolute measure, and thence the unit cell dimensions and volumes," p. 128.

In overgrowths "there is also the important case of the triclinic plagioclase feldspars, albite the soda feldspar $\text{NaAlSi}_3\text{O}_8$, and anorthite the lime feldspar $\text{CaAl}_2\text{Si}_2\text{O}_8$, the former having the molecular volume 100.1 and the latter the molecular volume 101.5. Zonal growths of one of these on the other are very common, often taking the form, as seen in rock sections, of regular bands surrounding a nucleus; and these two feldspars are the end members of a whole series of plagioclase feldspars containing both soda and lime, but they are not truly different minerals, although they have been given distinctive names, such as oligoclase, andesine, and labradorite, but isomorphous mixtures in different proportions of the two well-defined mineral species albite and anorthite, with optical properties of a distinctive character. 'Solid Solution' is a term, first applied by van't Hoff, which has been given to such close mixtures of isomorphous compounds, although the term appears to the author to be no more satisfactory than the so-called 'liquid crystal' term is for the curious liquids with which Lehmann has made us so familiar. But if by "solid solution" the idea is merely conveyed that the physical properties alter continuously with the chemical constitution, then it accords with the facts as derived from the results of the latest investigations, including the use of X-rays," p. 143.

"Some very interesting further facts, however, have been derived from the prolonged researches on mixed crystals. If we take, for instance, the case of the rhombic series of

alkali sulphates and selenates, the volume constants and cell-edge dimensions of which are given on pages 94 and 95, it is found that the two end members of either group, the potassium and caesium salts, which in the progression according to atomic number of the alkali metal are the furthest apart in regard to the relative and absolute dimensions of the space-lattice cells, never form mixed crystals at all, nor even any parallel growths or overgrowths. But the intermediate rubidium salt will form mixed crystals with either the potassium or the caesium salt, but with some difficulty, however, and parallel growths readily, the differences in cell dimensions being less in these cases. On the other hand, the ammonium and rubidium salts, which have been shown to be remarkably isostructural, will form mixed crystals with the greatest ease, and in all proportions. These facts are not only due to the author's observations; they were quite independently observed and published by T. V. Barker and by G. Wulff of Moscow. There is thus the fullest confirmation of their truth. That the absolute dimensions of the cells, as well as the relative sizes, in the cases of the rubidium and ammonium salts of the same group, are nearly identical was proved by the X-ray analysis of the crystals supplied by the author to Sir William Bragg, in whose laboratory the analysis was carried out as already described," p. 145.

"The question that has agitated most of the workers on the subject of mixed crystals has been whether the two substances which mix in the crystalline condition do so in alternating layers of the two substances—a view advocated by Retgers—or as a much more intimate intermingling, to form a crystal with intermediate angles and physical properties, as of one single substance. This latter view has been held by Wulff, Barker, Gossner, from work on the silico-fluorides and stannofluorides of zinc and nickel, and the author," p. 146.

"The matter has eventually been settled by X-ray analysis. Two independent X-ray investigations were carried out by Vegard and Schjelderup with mixtures of the cubic alkali halides, potassium chloride KCl, potassium bromide KBr, and ammonium bromide NH₄Br, and by Rinns with the rhombohedral carbonates, the cubic haloid salts of lithium, sodium, potassium, rubidium, and caesium, and several mixtures of metals. In all cases the mixed crystals were found to reflect X-rays as single entities, the spectra being, not double as from two different structures, but single and as clearly defined as for a pure single substance. The atoms of the two substances are probably most intimately disseminated throughout the structure, in the proportions corresponding to the relative quantities of the two substances present," p. 147.

"Pasteur somewhat later made the further remarkable observation that when the spores of the ferment *Penicillium glaucum* are added to a solution of racemic acid containing a small quantity of phosphates, which would appear to be essential to the life of the organism, the dextro component of the molecular compound is devoured by the organism, while the laevo component is unacted upon so long as any dextro remains. Why this selection occurs is one of the mysteries of life, but the fact is a fortunate one for enabling the laevo variety to be isolated, and it was thus obtained practically pure by Pasteur," p. 202.

"Pasteur was born on December 27th, 1822, and in December 1922 a paper was presented to the Royal Society by Mr. W. T. Astbury describing the successful X-ray analysis of tartaric acid, carried out in Sir William Bragg's laboratory, fully confirming the work of Pasteur and affording a remarkable insight into the crystal structure of the two varieties. Two asymmetric molecules C₄H₆O₆ were found to be contained in the unit cell of the space-lattice. The expected spiral structure was revealed, and in fact two spirals are present of different winding, but not mirror-images of each other. One is in the interior of the molecule itself, being associated with the four carbon atoms of the centre of the molecule, which are situated at alternate corners of the oblique parallelepiped; it therefore remains permanent when the crystal is dissolved in water, and causes the dextro-rotatory optical activity of the solution of ordinary tartaric acid. The other is a twist caused by the necessity of fitting the molecules in their places, and is associated with the four hydroxyl groups; it is thus a peculiarity of the crystal structure only. Being of inverse sign to the other, laevo-rotatory in the case of ordinary tartaric acid, and more powerful in its effect on light, it imposes, in the net result of the two rotations, its sign on the rotation of the plane of polarisation by the crystals. The two molecules in the cell are of the same variety, definitely

either right (in ordinary tartaric acid) or left (in the laevo acid), and not of the two different varieties, so that there is no internal compensation. The three accompanying figures illustrate the results," p. 204.

"The best explanation yet advanced as to the nature of 'liquid crystals' is due to Bose, and is known as the 'Swarm Theory,' which he propounded in 1907. It is practically based on the fact already commented upon, that the molecules are always very extended ones. If two such elongated molecules approach each other within half their length, their free rotation is prevented in all directions except that of their length, so that a more or less parallel position is necessarily assumed. A bundle or 'swarm' of such molecules arranged parallel-wise will have the symmetry of a rotation figure, and behave somewhat like a uniaxial crystal. Now no biaxial interference figure in convergent polarised light has ever been observed with 'liquid crystals.' This is the more significant as the vast proportion of organic compounds crystallise in the three biaxial systems, and more than fifty substances are now known exhibiting the phenomena of 'liquid crystals.' Each individual swarm will be clear and transparent, but between the swarms light will be scattered and the observed turbidity thereby caused. The molecules in a single swarm, when confined in the thin film between the micro-slip and the cover-glass, will all be arranged end on, all parallel to themselves and perpendicular to the glass plates. They will take up this attitude very readily, owing to molecular cohesion, and it is in this position that they afford the uniaxial interference figure in convergent polarised light," p. 224.

It would thus appear that 'Liquid Crystals' are not really crystals at all, but a highly interesting intermediate form of matter, in which the molecules are no longer free to roll about as in a liquid, and yet are not arranged in a crystal structure but merely in bundles parallelwise, owing to their length or extended nature and shape, and partly aided in many cases, doubtless, by their viscosity. The unusual play of molecular forces between such large and extended molecules would, of course, also be a powerful factor in producing swarms. The long controversy, which raged between Vorländer, who stood out even more strongly than the late Prof. Lehmann himself (who, unfortunately, died last year, 1924), for a space-lattice crystal structure, and Tammann, who utterly negated the idea of anything but an ordinary emulsion, is thus apparently happily settled, the truth lying, as so often happens, between the two extremes," p. 226.

Wilder D. Bancroft

Collected Physical Papers. By Sir Jagadis Chunder Bose. 25 × 15 cm; pp. ix + 404. London and New York: Longmans, Green and Co., Price: 10 shillings. This book contains a collection of papers on physical subjects by the author. Bose was quite early in the field of investigation of the properties of Hertzian waves especially in connection with waves of short wave-length. He devised apparatus of quite small dimensions (compared with the large-scale apparatus of Hertz and Lodge) by which the optical properties of such waves could be demonstrated. A number of these papers were published in the Proceedings of the Royal Society of London from 1895 onwards. Bose has also made investigations on the response of plants to stimulation and has exercised considerable ingenuity in devising apparatus for such enquiries.

In connection with the apparatus for indicating the growth of plants, some doubt may be felt as to whether he has taken sufficient precautions against expansion due to temperature change. When a linear magnification of 50 million times is obtained, fluctuations due to temperature variations must be expected to become very evident.

However this may be, the papers (as Sir Joseph Thomson remarks in a foreword) make very agreeable reading, for the author is never dull. Moreover they have contributed largely to develop in India an interest in physical investigations. This work was that of a pioneer and the present rapid growth in physical science in India is to a large extent the outcome of that work. This volume is a fitting record of it.

A. W. Porter

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VULCANIZATION OF RUBBER

BY NICHOLAS BACON

Introduction

Although vulcanized rubber articles have been in common use for more than three quarters of a century, nevertheless, the mechanism of the vulcanization process has never been satisfactorily explained. The rubber industry has recently grown to tremendous proportions. The introduction of organic accelerators has improved the physical properties of the rubber vulcanisate to such an extent that it has made possible the production of the modern automobile tire.

All the progress that the industry has made in improving the vulcanization process, has been brought about by empirical means. The "Edisonian" type of research that enabled Charles Goodyear to discover vulcanization is, even to this day, the system that is primarily employed in the rubber industry. Outside the classical work of C. O. Weber,¹ very few attempts have been made to study the subject of vulcanization from a systematic and scientific point of view. In studying the theories of vulcanization propounded by various investigators as outlined in a series of articles by Dubosc,² one immediately notices that the work of these investigators lacks coherence. Most of them draw sweeping generalizations from a small amount of experimental data confined to a narrow branch of the vulcanization problem, at the same time ignoring work performed in other fields of the same subject. Some of them seem to dodge the main issue of the problem. André Dubosc³ goes into elaborate detail in describing the formation of an active form of sulfur during the vulcanization process, but does not seem to be very much interested in what follows.

Things were in a rather chaotic condition until the advent of Wolfgang Ostwald⁴ in 1910. After surveying the results of the various investigators, and being an orthodox colloid chemist, he came to the conclusion that the available data were more in accord with a process of adsorption of sulfur by rubber than one in which sulfur entered into chemical combination. Ostwald's stand produced a beneficial effect in that it encouraged discussion and proved an incentive to further research on the subject of vulcanization. It helped rubber chemists to orient themselves so that the work undertaken was not done blindly. The issues of the subject were becoming plainly defined. Either chemical combination took place during the process, or it was simply a case of adsorption. From this one could deduce the possibility that it may be a combination of both.

¹ "The Chemistry of India Rubber," 91 (1902).

² Rubber Age, 16, June-December (1924).

³ Rubber Age, 16, 120 (1924).

⁴ Kolloid-Z., 6, 136 (1910).

Before discussing any of the existing theories of vulcanization, it would be advisable to define some of the terms connected with vulcanization. When a rubber-sulfur mixture is subjected to a temperature of about 120°-150°C for some time, one notices a gradual change in the physical properties of the product. The temperature limits are not well defined and are changed radically by the presence of various accelerators. The lower the temperature the longer it takes the product to attain the desired changes in physical properties. The original object of vulcanization was to decrease the effect of temperature changes on the rubber, since the raw rubber becomes sticky when hot. Apart from this, there are other very noticeable temperature changes. If a piece of unvulcanized rubber is stretched and then chilled in ice water, it remains stretched. A piece of vulcanized rubber, for example an ordinary rubber band, snaps back after receiving the same treatment. A piece of partially vulcanized rubber, particularly if vulcanized with ultra-accelerators, may appear to have at room temperature about the same properties as the well-cured rubber band; but it will retract very slowly in ice water after being stretched. Both the partially vulcanized and the unvulcanized rubbers resume their original shape, or very nearly so, when they are brought back to room temperature.

On vulcanization, the raw rubber mixture undergoes other decided changes, becoming more resistant to solvents, stretching, abrasion, and the action of chemical agents, and also increasing in strength. These desirable changes in physical properties may be brought about also by the use of other agents. When raw rubber is treated with a dilute solution of sulfur chloride, it is not necessary to heat the product in order to attain the desirable physical properties characteristic of a vulcanized product. Raw rubber has been successfully vulcanized with *m*-dinitrobenzene,¹ trinitrobenzene, and with similar compounds; but these products proved to be of academic interest only, and never were able to assume the commercial importance allotted to the two classical methods mentioned above. The term vulcanization as commonly used in the rubber industry, is really confined to the process that causes a change in the physical properties of a raw rubber mixture which makes the product useful commercially. Vulcanization may, therefore, be defined for practical purposes as the change in physical properties due to the action of sulfur, or sulfur monochloride on rubber. A complete theory of vulcanization must, of course, include the somewhat similar changes in properties produced by oxygen, selenium, etc.; but it is simpler and wiser to consider the sulfur vulcanization first and later to see how far the conclusions are applicable generally.

The word "cure" is very often used synonymously with the term vulcanization, but really designates a particular stage in the process of vulcanization that yields a product of commercial value. If a product has acquired the desired physical properties, it is said to be "properly cured." If it has not reached that stage, it is said to be "undercured," and when it is heated too

¹ Stevens: *J. Soc. Chem. Ind.*, 36, 107 (1917).

long, it is said to be "overcured." During the process of vulcanization some of the sulfur becomes firmly attached to the rubber, whereas the remainder can be extracted easily by suitable solvents. The sulfur held in firm combination is called "combined sulfur," and the percentage of combined sulfur present, based on the original amount of raw rubber, is called "coefficient of vulcanization." One must bear in mind that the amount of combined sulfur present is not a measure of the degree of vulcanization. The attainment of the physical properties characteristic of a properly cured rubber mixture depends to a great extent on the presence of foreign ingredients such as accelerators. By the use of some organic accelerators it is possible to produce a vulcanized sample containing much less than half of one percent of combined sulfur. Some of the physical properties of this sample may be far superior to those of any properly cured sample, not containing any accelerator and having a combined sulfur content of over three percent. It is, of course, possible that a large part of this variation in properties may be due to the milder heating conditions.

The use of accelerators in the vulcanization of rubber is a very important phase of the rubber industry. They perform two functions:

In the first place, they reduce the amount of heat necessary for the process of vulcanization. Some of them are quite effective at temperatures much lower than those formerly used.

In the second place, their use improves the quality of the product obtained. The chief aim in the early development of the industry was to use accelerators for the purpose of shortening the time of cure. At present, accelerators are selected also on the basis of added physical properties.

Now that we understand what is meant by vulcanization we can proceed to discuss some of the theories that have been propounded to account for the peculiar phenomenon. Weber¹ was the first to formulate a theory that was substantiated by adequate scientific experimental data. The fact that a portion of the sulfur was taken up by the rubber in such a way as to be no longer extractable by solvents for sulfur, was regarded as evidence that chemical combination had taken place. Since the reaction was not accompanied by the evolution of hydrogen sulfide, Payen² had suggested that the process was one of addition and not substitution. The limit of combination of rubber with sulfur was shown to be reached in the formation of a compound having the empirical formula $C_{10}H_{16}S_2$ (polyprene disulfide). Weber regarded this as the highest member of a series of polyprene sulphides the lowest member of which was a compound represented by the formula $(C_{10}H_{16})_{10}S$ containing 2.29% sulfur. This was assumed to be the lowest compound because the properties of vulcanization first became apparent when the combined sulfur was present to the extent of 2 to 2.5%. Weber assumed that it was impossible to obtain any evidence of the formation of separate members of this series of compounds, since the alteration in properties from unvulcanized to vulcanized soft rubber and then to hard rubber was a gradual

¹ "The Chemistry of India Rubber," 91 (1902).

² Compt. rend., 34, 2 (1852).

one, characterized by no sudden changes in any of its properties at any stage in the process.

While Weber's experiments indicated that the progress of vulcanization was accompanied by a chemical reaction, his explanation did not seem entirely adequate, since it was possible by use of accelerators, to vulcanize rubber with a smaller amount of sulfur than he had postulated for his smallest molecule $(C_{10}H_{16})_{10}S$. Weber's explanation accounts for the facts better than any other theory, but the main objection to it is that it is almost impossible to check it experimentally. By definition, it is assumed that the various members of the series of compounds formed are so closely related to each other in properties that it is naturally impossible to separate them.

A great many theories followed Weber's, but these may be regarded as the forerunners of the adsorption theory that was propounded by Wolfgang Ostwald in 1910. After considering all the results of previous workers, Wolfgang Ostwald sought to show that the available data were more in accord with a process of adsorption of sulfur by rubber than with one in which sulfur entered into chemical combination with the rubber. A very good discussion of the adsorption theory is found in Luff's book,¹ from which a good many of the facts have been taken. The chief facts on which his hypothesis was based were as follows:

- 1) In all vulcanized rubber there is present free sulfur which would not be expected if a chemical reaction were involved.
- 2) According to Höhn,² vulcanized rubber on sufficiently prolonged extraction could be freed entirely from sulfur.
- 3) The rubber always takes up sulfur in a purely additive manner.
- 4) A continuous series of addition products is formed, the first and last members of which have no definite stoichiometrical composition.
- 5) The amount of sulfur adsorbed by the rubber increases with the previous mechanical treatment. This could be explained by assuming rubber to consist of a two-phase system, the degree of dispersion of the disperse phase and hence the adsorptive capacity, being thus increased.
- 6) The capacity for taking up sulfur increases with rise in temperature and the temperature coefficient is more nearly in accord with an adsorption process.
- 7) The fixation of sulfur at a given temperature does not take place uniformly, as the breaks in Weber's curve show; this phenomenon is frequently met with in the adsorption of water by certain gels, for example silicic acid.
- 8) Adsorption proceeds in accordance with the exponential equation $x/m = kc^n$ where x is the weight of the adsorbed substance, m is the weight of the adsorbent, and k and n are constants.

The views put forward by Wolfgang Ostwald created a great deal of excitement and at the same time were a cause for further research which immediately established the inaccuracy of most of the facts upon which the adsorption theory was based.

¹ "The Chemistry of Rubber," 95 (1924).

² Gummi Z., 14, 17, 33 (1899).

With reference to the assumption that free sulfur is always present in vulcanized rubber, this is quite true with regard to the rubber heated with sulfur for a sufficient time to permit the characteristics of vulcanization to be assumed. It was shown, however, by Spence and Young¹ that on heating a mixture of 100 parts rubber, first extracted with acetone to remove resins, with 10 parts of sulfur for thirty hours at 135°C and ten hours at 155°C, respectively, no sulfur could be extracted on treatment with acetone.

Höhn's statements that all the sulfur could be extracted from vulcanized rubber failed to be verified by other workers. Stevens² cured a rubber mixture containing ten percent sulfur for thirty minutes at 145°C, and after nine weeks extraction with acetone, the sample still contained 1.55% sulfur. Other samples were treated in similar manner, but in all cases sulfur remained in the extracted sample even after nine weeks extraction.

In reference to the additive nature of the process, nobody ever questioned it after Weber's experiments showed the absence of hydrogen sulfide from the products of the reaction. The statements that none of the compounds formed by rubber-sulfur combination contained sulfur in stoichiometrical proportion was not in agreement with Weber's experiments, which showed that the highest limit of combination corresponded closely with the compound $C_{10}H_{16}S_2$. Spence and Young corroborated Weber's results by vulcanizing a rubber-sulfur mixture containing 63 parts rubber and 37 parts sulfur at 135°C for periods varying from one to thirty hours. At the end of 18½, 20, 25, and 30 hours the proportion of sulfur left in the residue after extraction of free sulfur was 31.75, 31.97, 31.91, 31.97 respectively. The samples after 20 hours vulcanization still contained about 4 percent free sulfur, so that the stopping of the reaction was not due to lack of sulfur.

The formation of an upper limit compound was further emphasized by Hinrichsen and Kindscher³ who heated rubber in cumene at 170°C with proportions of sulfur increasing to 400 percent, calculated on the rubber present. In all cases, a dark brown substance was obtained containing not more than 32 percent of combined sulfur.

With regard to the statement that mechanical working affected the rate of combination with sulfur, Weber⁴ had previously enunciated as a general principle that rubber containing a certain proportion of sulfur gave the same chemical result on vulcanization for a given time whether it had previously been subjected to mastication for a prolonged or normal period, although the physical properties might be widely different. Spence and Ward⁵ were able to corroborate these results. They found that the rate of combination of rubber with sulfur was the same whatever the mechanical treatment; but, in order to obtain products of equal tensile strength, it was necessary to vulcanize for a longer period in case of the over-milled sample than in the case of

¹ Kolloid-Z., 11, 28, (1912).

² J. Soc. Chem. Ind., 38, 195T (1919).

³ Kolloid-Z., 11, 191 (1912).

⁴ "The Chemistry of Rubber," 94 (1902).

⁵ Kolloid-Z., 11, 274 (1912).

the normally milled sample, and thus a higher coefficient of vulcanization was obtained.

According to Weber's results, the rate of fixation of sulfur at a given temperature was not uniform, and thus the breaks in the curve were held to support the adsorption theory. Of course, Weber himself suggested that the breaks in the curve might be interpreted as due to the formation of various chemical compounds, but finally decided that they had no such significance since these irregularities appeared at different places when vulcanization was carried out at different temperatures. He, therefore, concluded that they probably indicated a particular physical, rather than some definite chemical condition of the vulcanization product. Spence and Young repeated Weber's experiments, at the same time trying to eliminate all sources of error. They worked with acetone-extracted rubber so as to prevent the lack of uniformity that might result from the reaction of sulfur with non-caoutchouc substances proceeding at a different rate from that of the caoutchouc portion. Special care was also taken in reference to controlling the time of heating; and, in general, the technique governing the entire experiment was a vast improvement upon that of Weber's. Samples of a mixing of 90 parts rubber and 10 parts sulfur were heated at 135°C and various test samples were taken out at intervals. The combined sulfur was determined and the results obtained plotted against time of heating gave a smooth curve. A similar set of experiments was carried out at 155°C the results of which, likewise, produced a smooth curve when plotted.

The velocity coefficient k of the reaction was calculated from the equation $k = x/t$ where x is the percentage of sulfur entering into combination in time t . The temperature coefficient of the reaction velocity calculated from van't Hoff's equation was found to be 2.65 for ten degrees increase in temperature, a value agreeing with those generally obtained in case of a chemical reaction. Some experiments were performed at temperatures below 100°C and from this series, the temperature coefficient was calculated to be 2.84 which is within the limits characteristic of a chemical compound.

Further evidence in favor of a chemical combination is afforded by the experiments of Spence and Scott.¹ They found that when bromine reacts with vulcanized rubber, instead of combining in the ratio of four atoms of bromine for every $C_{10}H_{16}$, the resulting compound contains less bromine than required to form the tetrabromide, the balance being made up of the equivalent of sulfur.

Venable and Green² have shown that sulfur is quite soluble in rubber. This would naturally preclude the possibility of an adsorption complex between the sulfur and the rubber unless one made the unwarranted assumption that the sulfur suddenly crystallized out from solution and then became adsorbed on the rubber. This discussion of the theory of pure adsorption has brought forward an overwhelming amount of evidence in favor of the occurrence of a chemical reaction during the process of vulcanization.

¹ Kolloid-Z., 8, 304 (1911).

² J. Ind. Eng. Chem., 14, 319 (1922).

The controversy regarding the validity of the two classical theories naturally led to the formulation of theories that were to some extent a combination of both the chemical theory and the adsorption theory. Ostromuiskii¹ considers vulcanization as a process in which only a small proportion of the rubber enters into combination with sulfur to form a compound in which the unchanged rubber is swollen or adsorbed. The reverse condition may equally hold in which the compound formed is adsorbed by the unchanged rubber.

Axelrod² has assumed a process of polymerization in order to account for the change in physical properties. He claims that vulcanization is a process in which there occurs a simultaneous "depolymerization" by means of heat and a "polymerization" due to the sulfur with simultaneous formation of a sulfur addition product. It is not clear just what the author means by the term "polymerization." The term may refer to the chemical process of polymerization or it may be regarded as the reverse of the effect noted when rubber is submitted to mechanical working.

An explanation postulating a process of chemical polymerization or physical aggregation, or a combination of the two, is not a foolish one, since we may regard caoutchouc itself as a polymerization product of isoprene. This transformation has changed a liquid, soluble in many organic solvents, into an elastic substance which is insoluble in many liquids capable of dissolving the parent hydrocarbon. It is therefore, possible that caoutchouc itself may be further polymerized to form a product that is still more resistant to solvents, and with more marked elastic properties. So far all the agents that have been known to induce this polymerization (vulcanization) have at the same time entered into some sort of a chemical combination. Another objection to this theory is the fact that, once the polymerization has been brought about, it is impossible to reverse the process by depolymerizing the vulcanisate chemically so as to yield the original raw rubber.

Kirchhof³ has put forward a modification of the above theory in which he assumes vulcanization to be a transformation of the rubber from an unstable to a relatively stable form, the chemical combination of sulfur being regarded as a subsidiary process.

Of course, there are many more theories on the subject of vulcanization than those outlined above. Many of them are simply modifications of various phases of the above theories; some of them dodge the subject of vulcanization by expending their energies in accounting for an active form of sulfur, while others are of no use as working hypotheses since they are based on assumptions that would be almost impossible to submit to experimental verification.

Before investigating the subject of vulcanization any further, one should remember some of the well-established facts regarding the process of vulcanization that must be explained by any workable theory.

¹ Luff: "The Chemistry of Rubber," 103 (1924).

² Gummi Z., 24, 352 (1909).

³ Kolloid-Z., 13, 49 (1913); 14, 35 (1914); 26, 168 (1920).

In the first place, most people will agree that caoutchouc will combine with sulfur in the presence of an excess of the latter to form a definite chemical compound whose empirical formula is $(C_6H_8S)_n$.

When approximately 0.5% sulfur is mixed with raw rubber and the mixture subjected to the heating process of vulcanization, a tacky (sticky) mass is obtained that is similar to raw rubber subjected to the same heating process. All the sulfur may be held in firm combination by the rubber, but nevertheless the physical properties of the product are practically identical with those of the original raw rubber. No matter how long we may heat this product, it appears to be undervulcanized and resembles the raw rubber. As we increase the percentage of sulfur in the vulcanisate, the physical properties undergo change gradually. The change is a gradual, continuous, phenomenon until a region is reached in the neighborhood between a two and three percent sulfur content when the surface of the product is no longer sticky. At the same time the product becomes tougher and does not rupture readily on stretching. At this stage the product is said to be completely vulcanized. If heated too long, it becomes comparatively brittle and it is then said to be overvulcanized. When the various vulcanisates, mentioned above, are subjected to peptization with benzene, it is found that the low sulfur vulcanisates can be peptized completely and, as the sulfur content increases, it gradually becomes more difficult for the benzene to peptize the product completely. A stage is reached finally when some of the product can be peptized while the rest remains behind in the form of a swollen mass resembling solidified gelatine. And thus, as the sulfur percentage of the vulcanisate increases, less of the product is peptized by the benzene, until a stage is reached at which practically no peptization takes place. The benzene simply swells the rubber product. Stevens¹ has shown that even with vulcanized products containing as high as 8.64% combined sulfur, it was possible to peptize only about 13% of the product with benzene. It, therefore, follows naturally that complete insolubility in benzene must take place at a coefficient of vulcanization much higher than that just mentioned.

No matter what the method used in vulcanizing the product, there has always taken place a very strong union between all the rubber and some of the vulcanizing agent. All efforts to disrupt this union have resulted in complete annihilation of the rubber molecule. If a soft-rubber vulcanisate be prepared, it is possible to add a halogen until the difference between its stoichiometric composition and that of the upper-limit hard-rubber compound $(C_6H_8S)_n$ is satisfied. This would tend to indicate that the combined sulfur in the soft-rubber product is held in chemical union.

Whenever rubber is rolled on the mill, it becomes softer and more plastic. It is also peptized more rapidly by the ordinary solvents. After being milled, the rubber is said to have become "depolymerized." Sulfur is known to be fairly soluble in rubber at vulcanization temperatures, and as vulcanization proceeds the sulfur becomes more soluble.

¹ J. Soc. Chem. Ind., 38, 195 T (1919).

In studying the subject of vulcanization one should bear in mind improvements in the physical properties of a vulcanisate due to the presence of various fillers. Clays and various forms of carbon black are commonly used in the rubber industry. It has been observed that the particle size and the method used in preparation of the filler have an important bearing on the final physical properties of the vulcanisate. The method used in preparation of fillers has undoubtedly an important effect on their surface characteristics. Carbon blacks are used in tread stocks and are known to improve the strength and the abrasive qualities of the vulcanisate. This is probably due to the peculiar properties of surface adsorption common to various forms of carbon black. In this connection it might be mentioned that the use of accelerators improves the physical properties of the vulcanisate. This effect has not been ascribed to surface phenomena but to the fact that less heat is used in vulcanization when accelerators are present. Heat has a degenerating effect on a vulcanized product and naturally the less heat used in the process the more improved are the physical properties of the product.

In addition to the above facts, one must remember that it is possible, with the presence of powerful accelerators, to effect vulcanization even with coefficients of vulcanization less than 0.5% sulfur.

A knowledge of the ultimate structure of the rubber latex particle ought to be of some help in studying the subject of vulcanization. The latest work of Hauser¹ has shown that the latex globule consists of an outer skin a solid phase, evidently a high polymer of isoprene, and an inner liquid phase, evidently a lower polymer of the same hydrocarbon. Outside of the polymerized hydrocarbon skin is a layer of protein which plays the leading role in the coagulation process. It is interesting to note that x-ray researches on rubber have always indicated the presence of an amorphous phase. When the rubber is stretched, the presence of crystalline phase is also indicated. The presence of this phase is said to be due to the highly polymerized outer layer of the latex globule.

Although the formulation of the adsorption theory caused a great deal of activity in rubber research, nevertheless, the problem of vulcanization was not attacked in a comprehensive manner. Investigators have studied the various facts upon which both the adsorption theory and Weber's theory are based, but no attempt has so far been made by any single individual to study the vulcanization problem from every conceivable viewpoint. A person who has investigated a problem from all angles is always in position to have a better perspective view of the situation than one who has limited himself to a single phase of the question. His position enables him to weigh his evidence properly so that his final judgment becomes quite more reliable. Even Wolfgang Ostwald was forced to make some blunders in formulating his adsorption theory since he had done very little work on vulcanization and naturally was in no position to be able to weigh his evidence properly. The work undertaken in this investigation has been done with the idea of testing thoroughly

¹ Ind. Eng. Chem., 18, 1146 (1926).

every theoretical possibility that might be used in formulating a satisfactory vulcanization hypothesis.

Let us now consider all the theoretical assumptions that might be associated with a proper explanation of the vulcanization process. In the first place, we might think of the sulfur-rubber combination as simply a case of solid solution. If such be the case, it should be possible to extract some of the combined sulfur by treating the vulcanisate with an excess of raw rubber in a suitable solvent. We might also consider the process as simply adsorption or a combination of adsorption and a chemical compound. Either possibility could be verified by the same set of experiments. In either case, heterogeneity should become apparent whenever the soft rubber vulcanisate is subjected to fractional peptization in benzene. The first fractions to be peptized should show a low content of sulfur, while those following should naturally show a higher sulfur content. The reverse process of synthesizing a vulcanized product from raw rubber and a sample containing a high coefficient of vulcanization should likewise naturally follow. It is also possible to assume that the nature of the rubber is changed during the process of vulcanization and that the sulfur-rubber combination is simply a side issue. In that case, it should be possible to induce the change of vulcanization without any apparent participation on the part of the vulcanizing agent. So far, this has never been realized. Furthermore, it should be possible to reverse the change by obtaining raw rubber from vulcanized rubber; but this, likewise, has never been effected. As far as experimental evidence is concerned, we might just as well rule this possibility out. We might also look upon the rubber molecule as an unusually large one and capable of forming a series of compounds with sulfur. Let us assume the molecule of caoutchouc to be $(C_{10}H_{16})_n$, in which n happens to be very large. This is capable of combining with a small percentage of sulfur to form the compound $(C_{10}H_{16})_nS_2$. Further increase of the percentage of sulfur will produce the combination of $(C_{10}H_{16})_n(S_2)_2$, and thus progressively down the line until the maximum amount of sulfur is taken up with the production of the compound $(C_{10}H_{16})_n(S_2)_n$. If we should take n large enough the difference in properties of the various compounds would be so small as to preclude any possibility of separation. Thus there would be no abrupt changes in the physical properties of the products and all changes in properties would take place practically continuously. The above assumptions would be very difficult to check experimentally; but if, by chance, compounds happened to be formed at half percent intervals, or greater, it might be possible to notice some flat portions in the curve by studying the equilibrium relations between rubber and sulfur dissolved in some solvent in which the rubber is not appreciably peptized. We are now ready to proceed to the body of the investigation in which the above theoretical possibilities have been submitted to experimental verification.

Experimental Data

The various experiments performed during this investigation will not be discussed in chronological order, but will be grouped together under the

respective theories which they are designed to verify. Before describing the test for solid solutions, it would be well to detail the analytical procedure in the determination of sulfur in samples of vulcanized rubber. The author has used this method extensively for the determination of combined sulfur and has found it to be quite reliable.

A half-gram sample of extraction residue is placed in a 300 cc sulfur flask and 15 cc of saturated solution of arsenic acid is added. The saturated solution of arsenic acid is made by adding arsenic pentoxide to boiling water until the boiling point of the solution is 140°C . After the arsenic acid addition, 13 cc of fuming nitric acid, which has been standing over an excess of bromine, is added to the sample. The mixture is covered with a watch-glass and boiled on a hot plate until the sample is completely oxidized so that a clear solution is obtained, and, if necessary, more acid is added. The watch-glass is then removed, the contents evaporated to a syrup, and some crystals of potassium chlorate are added to expel the oxides of nitrogen. The evaporation is continued almost to dryness, cooled, and the residue is then taken up with 50 cc of hydrochloric acid (1:10). The flask is warmed until solution becomes complete, filtered, diluted to about 250 cc, and precipitated with barium chloride. The barium sulfate is filtered, ignited, and weighed in the usual manner. Blank runs should always be made on new lots of arsenic acid.

Test for Solid Solution

If the sulfur-rubber combination existed in the form of a firm solid solution, it should be possible to extract some of the sulfur by treating the vulcanisate with solvents in which the sulfur would be readily soluble.

Accordingly, 3 grams of the extracted hard-rubber, prepared as described in the next section, were added to 50 cc of aniline which contained 6 grams of raw rubber. Whenever the word "extracted" is used, it is understood to imply extraction with acetone. Aniline was chosen for the solvent because sulfur is very soluble in hot aniline and the latter is quite effective in peptizing raw rubber. The raw rubber was added to make the extraction more effective. It was thought that the raw rubber would combine with the sulfur extracted by the aniline, thus renewing the solvent action of the latter. The entire mixture was kept in a pressure bottle for fifty hours at a temperature of 190°C . The hard-rubber had been previously extracted thoroughly with acetone so that no free sulfur was present. The hot solution was then filtered several times and the filtrate evaporated to dryness. The sulfur content of the evaporated residue was then determined. Although the total amount of hard rubber present contained 0.6 gram of sulfur nevertheless there was only 0.04 gram sulfur left in the filtrate residue. The presence of the 0.04 gram sulfur was undoubtedly due to the passage of some of the hard rubber particles thru the filter paper. It is known that hot aniline is capable of peptizing hard rubber shavings to a certain extent.

Under the conditions of the experiment, sulfur is known to be very soluble in aniline, and since none of it had passed into the aniline-raw rubber mixture,

it stands to reason that the sulfur in the hard-rubber is held in a union that is firmer than one would expect from a solid solution. Hence this experiment proves the assumption of a solid solution as a theory of vulcanization to be untenable.

Tests for Adsorption and Chemical-Compound Adsorption Complexes

Mixtures without Accelerators

As mentioned in the introduction, the same type of experiments could be used to verify either of the above assumptions. Let us assume that a chemical compound is formed which corresponds to the product obtained as the upper limit compound in hard rubber, viz. $C_{10}H_{16}S_2$. The compound thus formed is either adsorbed by the rest of the raw rubber, or the latter is adsorbed by the compound, thus forming an adsorption complex that gives to the rubber product the property known as vulcanization. It can be seen from this hypothesis that it should be possible, starting with a mixture of 15% hard rubber and 85% raw rubber, and subjecting the same to a process that would encourage adsorption, to realize finally a vulcanized product.

Accordingly, seventy parts of pale crêpe rubber were mixed with thirty parts of sulfur on a hand-roller mill that had been designed for the purpose of rolling sheet metal. Although this was far from being an ideal method for preparing rubber batches, yet it served its purpose admirably. The mixture was then cured in a steel mould for twelve hours at 145°C . The hard rubber, thus prepared, was broken up into fine shavings by means of an emery wheel and then thoroughly extracted for one week with acetone in a Soxhlet apparatus. A mixture of 15 parts of the hard rubber raspings and 85 parts of raw rubber was made on the roller mill, and although it was kept in a steel mould for twenty-one hours at 150°C , it showed none of the physical properties of a vulcanized product. In fact, it was possible to separate the hard rubber from the raw rubber by peptization in benzene.

It was thought advisable to repeat the experiment using a solvent that can peptize both raw and hard rubber. Xylene was tried first but it was impossible to peptize the hard rubber. Cresol was then tested and found to be successful.

One and one-half grams of hard rubber were peptized in 125 cc of cresol by means of vigorous stirring and heating for four hours at the temperature of boiling cresol (about 194°C). Eight and a half grams of raw pale crêpe were peptized in 75 cc of cresol by stirring and heating at 150°C for three hours. While the latter was still hot, it was poured into the peptized hard rubber solution and the mixed sol was stirred continuously and heated at $160^{\circ}\text{--}170^{\circ}\text{C}$ for thirty-six hours in an effort to cause vulcanization. The solvent was then distilled off at reduced pressure, most of it going off at a temperature of 95°C (pressure of 15 mm of mercury). The last traces of the solvent were difficult to eliminate, so that it was necessary to keep the oil bath at a temperature of $180^{\circ}\text{--}210^{\circ}\text{C}$ for about twelve hours. On opening the apparatus, the bottom of the flask contained a hard, black, vitreous mass that looked like bakelite. The total weight of the product exceeded the entire

amount of the mixture that had originally been placed in the flask. Since a small stream of air had been bubbled through the flask during the distillation in order to prevent bumping, it is conceivable that oxidation might have taken place with the resulting formation of the resin. Accordingly, the experiment was repeated without allowing any air to bubble through the flask, but even then, the same type of resin was obtained at the end of the experiment. Obviously, the resin formation cannot be ascribed to oxidation by the air.

It was thought that the resin formation might possibly be due to the condensation of the rubber hydrocarbon with the cresol. Therefore, the experiment was repeated with just raw rubber and cresol. The result obtained was different from that observed in the initial experiment. It proved to be a viscous semi-solid. The fact that the product was different showed that something had not been considered. Reference was made to Beilstein's handbook and it was discovered that when cresol is heated with sulfur or sulfides it is capable of forming a dye. Hence, it was immediately assumed that the formation of the resin depended on the presence of sulfur.

It was known from previous experiments that pure pale crêpe and cresol did not produce a resin after the evaporation of the solvent. Likewise, a mixture of hard rubber, raw rubber, and cresol, after subsequent evaporation did not produce a resin. Since sulfur was known to combine with cresol, it was thought that this combination plus raw rubber, was responsible for the resin formation. Therefore, it ought to be possible to produce the resin by making a mixture of raw rubber, sulfur, and cresol, followed by distillation of the solvent. The product obtained in this manner was an amber-colored resin, similar to the one obtained in the previous experiment. Hence it was thought that the presence of sulfur was the cause of the resin. Accordingly, it was decided to extract all the hard rubber thoroughly. Hard rubber raspings were heated under reduced pressure so that the free sulfur was condensed on cool parts of the flask. This was continued for thirty-six hours followed by extraction in a Soxhlet with carbon disulfide for one hundred hours. Thereupon, it was followed by acetone extraction for forty-eight hours.

The thoroughly extracted hard rubber was now used in a 15-85 hard-rubber, raw-rubber mixture that was peptized in cresol. The procedure was the same as in the former experiments; likewise the result was the same. A similar experiment was performed, using a thoroughly extracted sample of soft rubber instead of the hard. The soft rubber had been made from a seven percent sulfur-rubber mixture. Here, likewise, the same type of resin was obtained. Naturally, it was concluded that the resin formation was due, perhaps, to the reaction between the rubber sulfide compound and the cresol or to the reaction between the cresol and free sulfur formed by the possible decomposition of the vulcanized rubber. The next experiment was therefore performed to see whether hard rubber decomposes at 190°C, forming free sulfur.

A sample of hard rubber was extracted with acetone for one week and then analyzed for its sulfur content. The sample was then heated to 190°C for one week in a flask at the reduced pressure. This flask contained a condenser

that would collect any free sulfur formed. After this prolonged heating, the sample was again extracted with acetone for one week and analysed for its sulfur content. No change in the amount of combined sulfur was noticeable. Evidently, no decomposition took place when the hard rubber was heated.

It was thought desirable to see what would happen when just sulfur and cresol were heated together with subsequent evaporation of the solvent. The final product was a resin similar to those obtained in all the previous cases. The distillate had a strong mercaptan odor. The resin was essentially a mixture of sulfur and tar together with a small amount of organic thio-compounds that would have been converted into a brown sulfur dye had the mixture been subjected to much more prolonged heating. When treated with acetone, the sulfur dissolved and a soft, viscous, semi-solid was left which was similar to the residue remaining when cresol alone was distilled. Thus, the resin obtained in all the previous experiments was simply a mixture of tar due to the cresol and whatever else happened to be in the solution. Since the resin was not a homogeneous product, probably no vulcanization had taken place and resort was made to other solvents in an effort to find one in which the residue could be more easily identified. Attempts were made to precipitate the rubber in cresol by adding other solvents, but these were rather unsuccessful. Alcohol, acetone, benzene, chloroform, acetic acid, methyl alcohol, carbon tetrachloride, toluene, and tetrachlorethane were tried but none of them proved to be effective. Later in this investigation, some experiments were performed in which it was possible to precipitate most of the rubber by the use of absolute alcohol and potassium hydroxide.

Cresol having proved troublesome, other solvents were tried, and it was found that hot aniline could peptize hard rubber shavings. The sol obtained in this case is not as finely divided as the one obtained with raw rubber in benzene but nevertheless, it was a colloidal suspension. A sol of hard rubber in aniline was treated with one of raw rubber with the ration of 15 parts of hard rubber to 85 parts of raw rubber. The mixture was stirred vigorously for twenty hours at 180°C and subsequently distilled at reduced pressure. The dark, gummy product did not appear to be vulcanized. When peptized with benzene, the hard rubber settled out showing that no vulcanization had taken place. Another experiment was tried in which a 15-85 mixture of hard and raw rubber was heated under pressure for four hours until the temperature was raised as high as 245°C. This is about sixty degrees above the boiling point of aniline. On examining the contents of the tube, the particles of hard rubber were found to be dispersed in the raw rubber gel. The aniline was evaporated off. The residue did not appear to be vulcanized and the raw rubber was separated by means of peptization in benzene. The above experiments seem to indicate that one cannot obtain a vulcanized product from mixtures of hard and raw rubber subjected to the treatment outlined above.

In this connection, it might be appropriate to mention a very interesting series of experiments performed by Weber¹ in 1894. This investigator per-

¹ J. Soc. Chem. Ind., 13, 14 (1894).

formed experiments similar to those outlined above with the exception, that, instead of hard rubber, he used the end-product obtained when raw rubber is treated with an excess of sulfur chloride.

Weber dissolved five grams of Para rubber in 1000 cc of benzene. To this he added five grams of sulfur chloride. In consequence of the great dilution, the reaction proceeded slowly, but after three hours standing, all the sulfur chloride had disappeared. The solution was left standing overnight and on the following morning 400 cc of it, representing two grams of raw rubber used, were treated with absolute alcohol and the polyprene sulfochloride that separated out was purified and analysed. It contained 23.78 percent sulfur, so that there was no doubt but that the India rubber was converted into the sulfochloride, $C_{10}H_{16}S_2Cl_2$, even in such a dilute solution.

To the remaining 600 cc of the above solution, 22.5 grams of pure rubber in 200 cc of benzene were now added, and the mixture strongly agitated. The gelatinous character of the mixture rapidly changed into that of an ordinary rubber solution. On pouring this solution into absolute alcohol, a voluminous precipitate very much like polyprene sulfochloride was obtained. This precipitate was separated from the supernatant liquid by filtration, the filtered residue repeatedly washed with warm alcohol, and then dried in vacuo. In this manner a rather elastic substance was obtained, which on analysis was found to contain 4.96% sulfur.

The question now arises whether this product really possesses the properties of vulcanized rubber. To determine this point the substance was placed in benzene. After eighteen hours, complete solution has taken place, the solution appearing somewhat turbid. It was strongly diluted and filtered through a hot-water funnel. The filtrate appeared to be clean. On the filter remained a residue that was repeatedly washed with warm benzene and then dried. It formed a whitish, easily friable, mass that contained 23.44 percent sulfur on analysis. There is no doubt that this substance represents the total quantity of polyprene sulfochloride that was mixed with the India rubber and this is further confirmed by the fact that the above mentioned filtrate contains not the slightest trace of chlorine or sulfur. "This result," as Weber stated, "is conclusive proof that a mixture of polyprene sulfochloride and India rubber possesses the properties to be anticipated for such a mixture, but *not* those of vulcanized rubber." He went ahead further and proved that a rubber product vulcanized with sulfur chloride so that the combined sulfur amounted to only five percent, was a homogeneous compound and behaved differently from the mixture that he obtained above.

For this purpose, 25.5 grams of pure Para rubber were dissolved in 100 cc of pure benzene. Three grams of sulfur chloride were added to this solution, mixed vigorously, and then left to stand. Very soon, the mass began to thicken, the reaction reaching its maximum after fifteen minutes. After several hours standing the jelly was thoroughly broken up by stirring, and the resulting pulp poured into absolute alcohol. The precipitate was filtered, the occluded benzene driven off, and the substance finally dried in vacuo. The dry product contained 5.11% sulfur and in this respect is therefore identical

with the mixture of polyprene sulfochloride and rubber. The elasticity of the new substance is far superior to that of the mixture, from which it further differs by its absolute insolubility in all solvents. Even an immersion of weeks at a time fails to soften it although considerable swelling takes place. This however, is also the case with the sulfochloride $C_{10}H_{16}S_2Cl_2$. "It is evident," said Weber, "that this substance containing only five percent sulfur has no unaltered India rubber and must be considered as a sulfochloride distinctly different from $C_{10}H_{16}S_2Cl_2$."

Some time ago, experiments were performed in this laboratory by Mr. Leo Larkin on vulcanization in solution in which very peculiar results were obtained. In fact, it was deemed advisable to repeat the work. He mixed raw rubber and sulfur in xylene in such proportions as to give four percent of sulfur. This was boiled by refluxing until it was thought that all the sulfur had combined with the rubber. The rubber was precipitated with absolute alcohol, and steam-distilled to remove all traces of the alcohol and xylene.

In his second experiment, enough sulfur was added to the rubber in xylene to reach 32%. This was refluxed as before until the reaction was believed to be completed, and then another portion of rubber in xylene was added so as to make the sulfur percentage equal to four percent. The refluxing was then continued again and finally the rubber precipitated as described in the first experiment. Mr. Larkin reported the products obtained in both cases to be identical. If the results of these experiments were true, they would naturally prove that it is possible to vulcanize mixtures of raw and cured rubber, a thing which has never been done before. But it is quite possible that since vulcanization is slow in solution, practically no reaction had taken place in either of the above experiments. Therefore, his products would appear to be identical, with the net result that nothing spectacular had been proved.

The work was repeated as follows: 15 grams of pale crêpe were peptized in 100 cc of xylene. Likewise, 0.75 grams of sulfur were dissolved in a similar amount of xylene. The two solutions were mixed, thus forming a 5% sulfur-rubber mixture, and refluxed in an oil bath for seventy-five hours. After the solvent was evaporated under reduced pressure, the residue was examined and found to be unvulcanized. The combined sulfur amounted to about 0.6%.

Ten grams of pale crêpe were peptized in 100 cc of xylene and this was mixed with 3 grams of sulfur dissolved in 100 cc of hot xylene. The percentage of sulfur in reference to the raw rubber amounted to 30%. The entire mixture was refluxed about ten hours when particles of vulcanized rubber began to separate out. After a total of forty-six hours of refluxing, a sample of the rubber was taken out for analysis. It showed a combined sulfur content of 21%. Fifty grams of raw rubber were then added to the flask, thus bringing the original sulfur content down to five percent. The refluxing was resumed for twenty-nine hours more, the solvent distilled off as in the previous experiment, and the residue was found to be a mixture of vulcanite, raw rubber, and sulfur. The raw rubber was separated by peptization in

benzene. After evaporating off the benzene, the sulfur was separated by extraction with acetone. These experiments proved that nothing miraculous had happened. Mr. Larkin had been mistaken in that he had not refluxed his mixtures long enough to cause any appreciable combination between the sulfur and the rubber.

Mixtures containing Accelerators.

Thus far all the experiments have been performed without the use of any accelerators. Since accelerators are quite effective in facilitating vulcanization, it stands to reason that it would be a good idea to add them to mixtures of the type that we have been studying in an effort to see whether any desirable effect might be induced. Most accelerators act more effectively in conjunction with zinc oxide, hence the latter was added to some of the mixtures.

About 12.75 grams of pale crêpe were mixed with 2.25 grams of extracted hard-rubber raspings on the roller mill, and the resulting product divided into six portions. To each 2.5 gram sample of the hard-raw rubber mixture were added zinc oxide and the various accelerators as shown in Table I.

Grasselerator 808 is an accelerator containing no sulfur; it is butylidene aniline.

D. O. T. G. is di-ortho-tolyl-guanidine.

Monex is an ultra accelerator; tetra-methyl-thiouram-monosulfide.

TABLE I

| | |
|------------------------------------------------------------------------|--------------------------------------------------------------|
| Sample No. 1 6% Grasselerator 808 (.15 gr.) and 6% zinc oxide | Sample No. 2 6% Grasselerator 808 and no zinc oxide |
| Sample No. 3 6% D. O. T. G. and 6% zinc oxide | Sample No. 4 6% D. O. T. G. and no zinc oxide |
| Sample No. 5 6% Monex and 6% zinc oxide | Sample No. 6 6% Monex and no zinc oxide |

All the ingredients, outlined above, were mixed in separate batches on the roller mill. These were placed in a steel mould and heated at 140°C for three hours to see whether any vulcanization would take place. All the samples failed to exhibit the physical properties of a vulcanized sample. When peptized in benzene, the zinc oxide and the hard rubber settled to the bottom of the flask.

The next step was to see whether the same samples could be vulcanized in solution. Two-gram portions of each of the six samples were respectively peptized in 20 cc of cresol. They were heated for twenty-four hours at a

temperature of 150°-170°. Seventy-five cc of absolute alcohol were added to each of the samples in an effort to precipitate the peptized rubber. It was found that the hard rubber and zinc oxide were thrown out of suspension but that the raw rubber remained in colloidal solution. The hard rubber and zinc oxide were filtered off and 20 cc of a concentrated solution of potassium hydroxide were added to each of the filtrates in an effort to coagulate the raw rubber. It was possible in this way to precipitate some of the raw rubber but not all of it.

Since all the ingredients in the above mixtures could be separated, undoubtedly no vulcanization had taken place.

The above series of experiments were repeated, using a soft-vulcanized rubber instead of hard rubber. Two parts of raw rubber were mixed with one part of soft rubber containing 2.8% sulfur (combined). Accelerator and zinc oxide were added in the same proportions as in the previous set of experiments. The results obtained were likewise similar to those obtained with the hard-rubber mixtures.

Fractional Peptization Tests

If, during the process of vulcanization, compounds are formed between sulfur and caoutchouc, it should be possible to test the homogeneity of the product by fractional peptization. The first fractions should have percentages of sulfur that differ from those which follow. Hence it ought to be possible to separate a vulcanized product into the supposedly unattacked raw rubber and the product resulting from the chemical union between the sulfur and the hydrocarbon. Some work along this line has been done by Stevens¹ but he did not go far enough. The lowest combined sulfur content in his vulcanisate was 3.8%. He extracted his vulcanisate sample exhaustively with benzene for one week and determined the proportion of the sample dissolved by the benzene. The sulfur present in the sample before extraction and that left after extraction was determined. The following result was obtained:

| Proportion dissolved by benzene | Before extraction | Sulfur content after extraction |
|------------------------------------|-------------------|------------------------------------|
| 30.8% | 3.80% | 3.85% |

These results show that the vulcanized product is homogeneous as far as the sulfur content is concerned; the peptized portion containing the same amount of sulfur as that which was left after extraction. The question now arises whether this homogeneity will persist with vulcanized products containing much less combined sulfur than the sample studied by Stevens. With this in view, the following rubber mixtures were prepared:

Thirty grams of pale crêpe were mixed on the roller mill with 0.6 gram of accelerator (about 2% of Grasselerator 808). The resulting mixture was divided into four portions. To the first 5-gram portion was added 0.075 gram of sulfur, the resulting mixture being worked on the roller mill. This corresponds to an approximate sulfur content of 1.5%.

¹ J. Soc. Chem. Ind., 38, 195T (1919).

The second 5-gram portion was treated in a like manner with 0.05 grams of sulfur (about 1%).

The third 5-gram portions was mixed with 0.025 grams of sulfur (about 0.5%).

The last portion, amounting to fifteen grams, was treated with 0.015 grams of sulfur (about 0.1%).

All of the above portions were vulcanized in a steel mould for five hours at a temperature of 140°-150°C. The samples were then extracted for two days with acetone to remove all the free sulfur.

A day after the extraction, the batches were heated in the oven at 100°C to make certain that all the acetone had been driven off. The samples were then analysed for their respective combined sulfur values. Each of the above batches was then placed in a Soxhlet apparatus and subjected to peptization by hot benzene. Various fractions were thus obtained and each of these was dried free of solvent and the sulfur content determined. The results obtained are given in Table II.

TABLE II

| | Original Sample | First Fraction | Second Fraction | Third Fraction |
|---------------------------|-----------------|----------------|-----------------|----------------|
| First Sample | | | | |
| Weight of Sample Analysed | 0.5000 gms | 0.5488 gms | 0.3235 gms | 0.2283 gms |
| % Sulfur | 1.42 | 1.37 | 1.30 | 1.39 |
| Second Sample | | | | |
| Weight of Sample Analysed | 0.5405 gms | 0.4980 gms | 0.3524 gms | 0.4100 gms |
| % Sulfur | 0.75 | 0.72 | 0.80 | 0.77 |
| Third Sample | | | | |
| Weight of Sample Analysed | 1.0139 | 0.7192 | | 0.8024 |
| % Sulfur | 0.43 | 0.42 | | 0.39 |
| Fourth Sample | | | | |
| Weight of Sample Analysed | 3.9250 | 3.6072 | 3.7638 | 4.4677 |
| % Sulfur | 0.091 | 0.09 | 0.08 | 0.085 |

The above results show that homogeneity as far as sulfur content is concerned, persists even with samples containing less than 0.1% of combined sulfur. To be sure, all of the "vulcanized" products shown in the previous tables did not exhibit the physical properties common to a completely cured product. All the samples were heated for five hours at a temperature between 140° and 150°C. This is more than sufficient to vulcanize any product, but since they did not contain sufficient sulfur, they appeared to be undercured

even though the sulfur which they did contain was in complete union with the rubber. Such being the case, it was thought advisable to verify Weber's contention that the properties of vulcanization first become apparent at a vulcanization coefficient of from 2 to 2.5%.

Accordingly, three samples were prepared each of which contained about 2% accelerator (Grasselerator 808). About 2% sulfur was added to the first sample, 2.5% to the second, and about 3% to the third. All were heated in a steel mould at a temperature of 140°-150°C for five hours. The samples were taken out for examination and it was noticed that the one containing about 3% sulfur was definitely overcured. The other two cases were doubtful. It was known definitely that a sample containing 1.5% sulfur appeared undercured under similar circumstances, and since the 3% sample was overcured, Weber was right in his contention that signs of vulcanization are first noticeable with samples when they contain from 2 to 2.5% sulfur. Although Weber is probably correct when the samples which are free from any powerful accelerators are considered, nevertheless it has been possible in this laboratory to produce with the aid of zinc oxide and ultra-accelerators vulcanized samples of rubber that were cured at boiling water temperature and contained a sulfur content slightly less than 0.5%.

Experiments with Protein-Free Rubber

Since each globule in a piece of rubber is surrounded by a film of protein, it was thought that adsorption might take place much more readily if no protein were present. Therefore, steps were taken to prepare some protein-free rubber. The rubber was first extracted thoroughly in acetone for one week. Then it was placed in petroleum ether and allowed to stand quietly so that the hydrocarbon was slowly peptized. From time to time, the supernatant liquid was siphoned off carefully and evaporated to dryness. The rubber prepared was free from protein, but the process used was a very tedious one. It is much easier to dissolve the rubber in chloroform and to precipitate the hydrocarbon with alcohol. A sample of this protein-free rubber was mixed with sulfur and vulcanized so that the coefficient of vulcanization was about 2.8%. A gram of this vulcanisate was peptized in hot aniline and then a gram of raw rubber was added to the solvent and thoroughly mixed. The mixed sol was heated at the boiling temperature of aniline for twenty-four hours, after which the solvent was evaporated off at reduced pressure. The residue was then subjected to fractional peptization in benzene. The following results were obtained:—

| | Weight of Sample | % Sulfur |
|----------------|------------------|----------|
| First Fraction | 0.4188 grams | 1.1 |
| Second " | 0.311 " | 1.4 |
| Third " | 0.4945 " | 1.8 |
| Fourth " | 0.241 " | 2.0 |

The results of the above experiments show that the residue was not homogeneous and that the protein extraction was of no avail for inducing vulcanization between mixtures of raw and cured rubber.

Rubber Mixtures with Closely Related Coefficients of Vulcanization

Heretofore, the components of the rubber mixtures used, consisted of widely divergent coefficients of vulcanization. Raw rubber having a zero coefficient was mixed with hard rubber having a coefficient somewhere above twenty percent. Of course, when soft rubber mixtures were treated, the coefficients were much more closely related, but still there was quite a difference. Hence, it was thought desirable to test some mixtures in which the coefficients did not differ by more than 0.5%. Accordingly, two rubber batches were prepared which showed after vulcanization the following percentages of combined sulfur:—

| | |
|-------|--------------|
| No. 1 | 0.37% sulfur |
| No. 2 | 0.57% " |

Five grams of the first sample were peptized together with an equal amount of raw rubber in boiling xylene and refluxed for three days. The solvent was then distilled off and the residue subjected to fractional peptization with benzene. Likewise, five grams of the first batch were similarly treated with five grams of the second vulcanisate and the peptized mixture refluxed for three days in xylene. Here, likewise, the solvent was distilled off and the residue subjected to the same treatment as in the previous case. The following results were obtained:—

| | Mixture of raw rubber and 0.37% vulcanisate | Mixture of 0.37% and 0.57% vulcanisates |
|----------------|---------------------------------------------------|-----------------------------------------------|
| First fraction | 0.13% sulfur | 0.38% sulfur |
| Second " | 0.17 " | 0.39 " |
| Third " | 0.34 " | 0.47 " |
| Fourth " | 0.35 " | 0.54 " |

The above results clearly show that even in cases such as listed above in which the coefficients of vulcanization are very closely related, it is impossible to produce a homogeneous product from mixtures. Even in the last mixture in which the coefficients differed by only 0.2%, it was quite obvious that the product lacked homogeneity and that separation had occurred.

Fractional Peptization with Low-Temperature Vulcanisates

Since the average vulcanization temperature is far above the melting-point of sulfur, the latter is in a liquid state previous to its reaction with the caoutchouc. The fact that it is a liquid state helps it to diffuse through the rubber more readily and thus distribute itself uniformly throughout the rubber before actual vulcanization sets in. It was thought that if vulcanization could be induced at a temperature below the melting-point of sulfur, it might be possible to produce a heterogeneous product in which parts of the rubber in close proximity to particles of solid sulfur would be more vulcanized than other regions. In order to produce vulcanization at a temperature of

boiling water, it was found necessary to mix the rubber with about 3% zinc oxide and a quarter of one percent of an ultra-accelerator such as tetramethylthiouram-monosulfide. About half of one percent of sulfur was used in the above mixture. Part of the above batch was cured for thirty minutes in boiling water, and the other part was cured at the same temperature for one hour and three quarters. If the time of vulcanization was continued for two and one half hours, the sample became fully cured. That is, the physical properties of a completely vulcanized sample became apparent. After vulcanization, the samples were extracted with acetone for two days and then subjected to fractional peptization in benzene. The results were as follows:—

| | | |
|----------------|--------------|---------------|
| | 30 min. cure | 105 min. cure |
| First fraction | 0.21% sulfur | 0.51% sulfur |
| Second " | 0.19 " | 0.51 " |

These data show that in both cases the products are homogeneous and that the sulfur is quite soluble in the rubber even at temperatures below its melting-point. The natural corollary of this experiment is that sulfur in the solid state does not react with caoutchouc. It reacts with the rubber when it is either in solution or in the vapor phase.

Test for Giant Molecule

It is theoretically possible to consider an entire piece of rubber as one huge molecule. If such be the case, it should be possible, when a piece of new rubber is covered with sulfur and vulcanized, to establish heterogeneity in the product by cutting it into various sections, as one would do with a knife. Some of the sections, thus separated, should show very high percentages of combined sulfur while other parts should be practically free of any sulfur. On the other hand, if such a product were to be tested by means of fractional peptization in solvents, it would be impossible to peptize part of the giant molecule-sulphur compound without peptizing it all. In other words, all the various fractions of peptization must show the same sulfur content.

In order to verify the above assumption, fifteen grams of rubber were rolled into a sheet of about three-sixteenths of an inch in thickness. The upper surface of this sheet was covered with four grams of sulfur which was equivalent to thirty percent of the weight of the rubber used. The sheet was then placed in a steel mould and vulcanized at 150°C for three hours. After vulcanization, samples for analysis were taken from the upper and lower surfaces of the vulcanisate. They were first extracted with acetone and then analysed for combined sulfur. The sample from the upper surface showed a vulcanization coefficient of 9.5, while that of the lower surface could only boast a mere 3.2. When submitted to fractional peptization, this product could be separated into fractions, containing radically varying amounts of combined sulfur. The fact that heterogeneity was apparent when the product was submitted to fractional peptization is proof that the assumption of considering a piece of rubber as a giant molecule is untenable.

Tests for Chemical Compounds

Thus far, we have studied the problem of vulcanization from every conceivable angle, but have not as yet attacked the problem of the equilibrium relations existing between raw rubber and sulfur dissolved in a suitable solvent. In fact, the only experiments that have been performed along this line were confined to a study of the amount of sulfur taken up by raw rubber from a bath of molten sulfur. In this case equilibrium resulted with the formation of the hard rubber compound, $C_{10}H_{16}S_2$, containing 32% sulfur. For the success of this experiment, it was essential to find a solvent capable of dissolving sulfur but at the same time being void of any peptizing effect on raw rubber. Normal butyl alcohol, although not ideal, proved to be the best available solvent for this purpose. At the boiling point of butyl alcohol, the rubber softens and is very slightly peptized, nevertheless it served the purpose.

About twenty grams of raw rubber were extracted exhaustively with acetone. It was thought best to free the rubber from all resins so that a study could be made of the equilibrium relations between the sulfur and the caoutchouc without the presence of the disturbing influence of the resins. Realizing that it would take very long for equilibrium to be reached at the temperature used in the experiment, 0.4 grams of accelerator (Grasselerator 808) were used. This was mixed with the 20 grams of extracted rubber on a roller mill, and drawn out into thin sheets of about 2mm thickness. These sheets were cut into strips of about 3 to 4mm in width. Half gram samples of these strips were weighed carefully, and wrapped around glass drums. While wrapping, the strips were stretched to provide more surface with the net result that their final thickness amounted to about 1mm. Each of the glass drums containing half gram samples of rubber were placed in long tubes (200 × 20 mm) each of which contained 30 cc of n-butyl alcohol. After the necessary amount of sulfur had been added to each test tube, they were sealed off and placed in a n-butyl alcohol bath that was continuously refluxing so that a constant temperature of 117°C was maintained. Table III shows the concentration of ingredients used in the various test tubes:—

TABLE III

Each of the test tubes contained 30 cc of n-butyl alcohol and 0.5 grams of rubber.

| 5 tubes contained | 0.01 grams of sulfur each |
|-------------------|---------------------------|
| 4 " " | 0.025 " " " " |
| 4 " " | 0.06 " " " " |
| 4 " " | 0.12 " " " " |
| 4 " " | 0.2 " " " " |
| 5 " " | 0.5 " " " " |

After the first week's refluxing in the n-butyl alcohol bath, some of the samples were analysed to see how much sulfur had been taken up from the solution by the rubber. These test tubes were to be taken out from time to

time and analysed to see whether or not equilibrium had been attained. The samples taken out for analysis were treated as follows:—

On cooling, the test tubes were opened, the solvent distilled off at reduced pressure, so that the temperatures of distillation were less than that of the boiling butyl alcohol (117°C). Otherwise, the equilibrium might be disturbed if too high a temperature of distillation were used. The sample was then extracted with acetone for two days to remove all the free sulfur. The rubber was then analysed for the combined sulfur content.

After the first week's refluxing, a sample of the tubes containing the largest amount of sulfur showed on analysis that enough sulfur had been taken up to form a vulcanisate with a combined sulfur content of 29%. After three weeks' refluxing, another sample of the same type showed 32.4% sulfur. In other words, the sample had already reached the upper limit of chemical combination.

In a like manner, after the first week, a sample of the tubes containing the smallest amount of sulfur showed that the rubber had taken up 0.0048 grams of sulfur. This is slightly less than half the available sulfur present (0.01 gm.) After three weeks, it showed 0.0081 grams of sulfur in combination. A month later, another sample of the same tubes was analysed and showed a value that was just slightly less than the previous value reported. Obviously, equilibrium had already been attained. It took a longer time for the other concentrations to reach equilibrium, but all of them reached this point finally within the time used for refluxing the samples. Some of the samples were refluxing for about two and one half months. As they became more highly vulcanized, the rate of diffusion of the sulfur was correspondingly decreased so that it may finally have become slow enough not to be noticeable, although true equilibrium had not been attained. Thus no one could say with certainty whether or not true equilibrium had been reached. Venable and Green have reported that, in their determinations of solubilities of sulfur by rubber by diffusion of pure sulfur, it was impossible to obtain any solubility values with coefficients of vulcanization beyond seven percent, since the rate of diffusion of sulfur became practically zero.

The rubber samples were wrapped around the glass drums to provide greater surface area, but this was entirely nullified during the long process of heating, since all the rubber gradually sagged to the bottom of the test tube. Probably some of it had been peptized. This likewise, slowed up the process of sulfur diffusion. The test tubes with the largest concentration of sulfur

TABLE IV

| Initial amount of sulfur in tube | Conc. per cc of alcohol | Amount of sulfur combined | Combined S per gram of rubber |
|----------------------------------|-------------------------|---------------------------|-------------------------------|
| 0.01 gram | 0.00033 | 0.008 | 0.016 |
| 0.25 | 0.00083 | 0.020 | 0.040 |
| 0.06 | 0.002 | 0.045 | 0.090 |
| 0.12 | 0.004 | 0.080 | 0.160 |
| 0.2 | 0.0067 | 0.127 | 0.254 |
| 0.5 | 0.0167 | 0.242 | 0.484 |

had more of it than necessary to saturate the 30 cc of n-butyl alcohol, whereas the others were able to dissolve their quota of sulfur without leaving any excess at the bottom. The following are the equilibrium values obtained with the various concentrations used in the experiments:—

Each sample contained 0.5 grams rubber and 30 cc of n-butyl alcohol besides the various amounts of sulfur as indicated in Table IV.

In Fig. 1, the amounts of combined sulfur per gram of rubber are plotted against the initial concentration of the sulfur in the alcoholic solution. The curve obtained, starts out as a perfectly straight line and then bends very

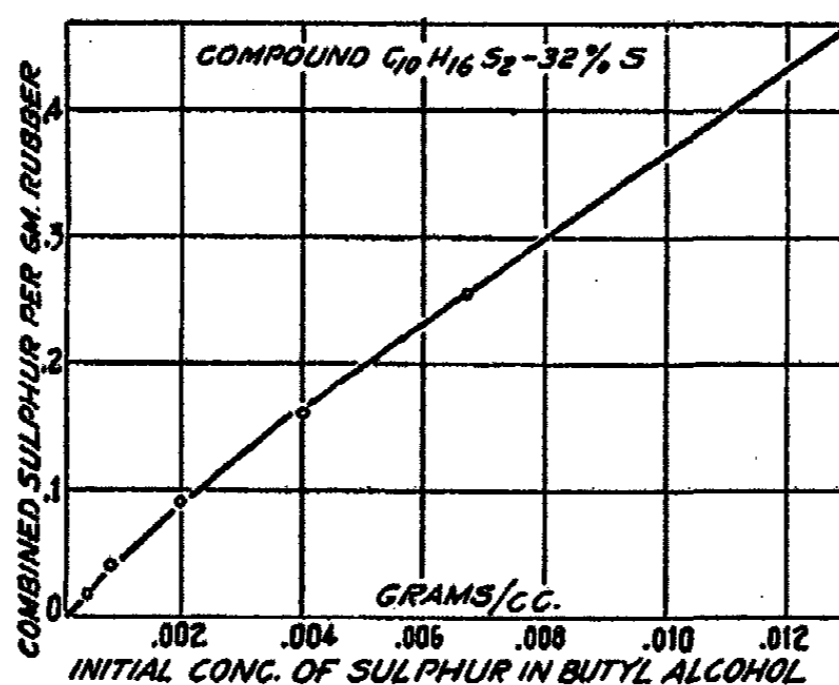


FIG. 1

slightly away from the vertical axis. It continues, undoubtedly, until it strikes the horizontal line indicating the upper-limit hard-rubber compound containing 32% sulfur. It is regrettable that so few high concentrations had been selected in planning the experiment. Otherwise, the curve would have appeared much more complete in that region. There is only one point to indicate the formation of the upper limit compound $C_{10}H_{16}S_2$, but that is not important since it is already a well-known fact. The author was especially interested in the soft-rubber region so that most of the concentrations selected were in that zone. It is quite obvious from looking at the curve that there is not the slightest trace of formation of any chemical compounds until the thirty-two percent compound is reached. We can also see that the amount of sulfur taken up is practically directly proportional to its concentration.

When you come to think of it, it is quite possible that all the values in the above experiment represent a condition of a false and not a true equilibrium. Spence and Young¹ have shown that, on heating a ten percent sulfur-rubber mixture for thirty hours at 135°C, there was no free sulfur left. It stands to reason, therefore, when a strip of rubber is immersed in a dilute sulfur solution of butyl alcohol and heated, that all the sulfur should be taken up completely by the rubber if the process of vulcanization be prolonged

¹ Kolloid-Z., 11, 28 (1912).

for a sufficiently long period of time. At vulcanization temperatures, sulfur is quite soluble in rubber. As the sulfur combines with the rubber, more of it should naturally diffuse into the rubber from the butyl alcohol. It is also known that sulfur is more soluble as the coefficient of vulcanization is increased. This, likewise, should increase the rate of sulfur depletion. Theoretically, this transfer of sulfur should go on until all the sulfur is gone unless enough sulfur is present to produce the upper-limit hard-rubber compound $C_{10}H_{16}S_2$.

To counteract the above efforts for complete elimination of the sulfur, we have the fact that, with progressive vulcanization, the diffusion of the sulfur becomes slower until it finally becomes zero with coefficients of vulcanization beyond seven percent. The temperature at which the experiments were conducted ($117^{\circ}C$) is a very low temperature for proper vulcanization so that the reaction proceeded at an unusually slow rate. The net result of the above opposing actions would be to create a static condition which might be classified as a false equilibrium.

Conclusion

After subjecting all the possible theoretical assumptions for a theory of vulcanization to experimental verification, we are now ready to correlate our results and to eliminate those considerations which experiments have shown to be unwarranted.

In the first place, it has been shown, quite obviously, that the process of vulcanization cannot be interpreted as a solid solution of the sulfur in the rubber.

The discussion in the introduction has discredited quite effectively the hypothesis of pure adsorption. The assumption of a chemical compound linked together with an adsorption process is a much more reasonable one. However, when this theory was subjected to proper experimental verification, it likewise failed. The natural inference, on the basis of this theory, was that it should be possible to synthesize a vulcanized product from mixtures of raw and vulcanized rubber. The reverse of this, the ability to detect heterogeneity by fraction peptization, should likewise naturally follow. Both these deductions failed to materialize experimentally. Hence, we cannot lay much faith in a theory of this type.

It is not necessary to mention the objections to the supposition that the nature of the rubber is changed during vulcanization since they have been explained in the introduction.

We cannot receive much comfort from the experiments on the equilibrium relations since we are not absolutely certain that the values obtained are representative of true equilibrium. Nevertheless, the curve obtained is practically a straight line without any intimation of the possible existence of any compounds with a sulfur content of less than thirty-two percent. If there did exist some compounds, let us say at one or two percent intervals, the author thinks it quite safe to assume that they would have been easily discernible by the work performed in this experiment.

Of course, the experiment on the existence of a giant molecule showed clearly that we cannot consider a piece of rubber as one single molecule. Likewise, the experiments on fractional peptization have shown that homogeneity persists even in vulcanisates with as low a coefficient of vulcanization as 0.1%. This would naturally imply that if chemical combination were assumed, a molecular weight of close to 32,000 would be the smallest that we could ascribe to caoutchouc for the purpose of forming the compound $(C_5H_8)_{470}S$, containing 0.1% sulfur. Work along this line has been done, showing that it is possible, by fractional peptization, to separate a mixture of two different vulcanisates in which the coefficients of vulcanization differed by 0.2%.

Now that we have considered all phases of the subject we are in a better position to offer an explanation of the vulcanizing process. All the work done so far, proves unquestionably that the nature of the union between the rubber and sulfur is a chemical one. Weber's theory thus far has been the most satisfactory. Of course, the very nature of his theory is such that one cannot subject it to experimental verification. He assumes that the series of compounds formed are so similar to each other that it is impossible to separate them. Nevertheless his theory explains things beautifully. It accounts for the gradual change in physical properties with progressive vulcanization. Although the best in its time, it needs only a very slight modification to enable it to account for all the facts known today. We must be able to account for the fact that it is possible, by the use of ultra-accelerators, to vulcanize rubber with coefficients of vulcanization much lower than Weber had assumed for initial compound containing 2.29% sulfur. Now that we have discarded the initial compound of Weber's series, it is necessary to find another one that is justifiable by some experimental proof in heading an analogous series of compounds. In selecting the proper size for the caoutchouc molecule, it has already been shown that the giant molecule is too big and that homogeneity persisted with vulcanisates containing as low as 0.1% of sulfur. Of course, experiments might have shown that homogeneity persisted even with vulcanisates containing less sulfur, but then it would be impossible to check this experimentally, since the analytical chemistry is not that accurate. Therefore, it is conservative to postulate that the molecular weight of the caoutchouc is at least 32,000 in order to account for the initial compound of a series that would extend up to a compound containing 32% sulfur. This initial compound must account for a sulfur content of 0.1%. Hence its formula would be about $(C_5H_8)_{470}S$.

In recapitulation, one might say without hesitation that the essential ideas embodied in Weber's theory are still effective in offering the best explanation of the vulcanization process. The introduction of a new series of compounds starting with a sulfur composition of 0.1% increases the value of n in the general formula $(C_5H_8)_nS$, so that the compounds formed are much more closely related to each other in physical properties than they were in Weber's original series. Thus, the very idea which he tried to stress in postulating his series of compounds becomes much more emphatic when the series is changed to account for new facts.

Acknowledgment

The author wishes to express his appreciation to Professor W. D. Bancroft for his guidance and hearty cooperation in rendering possible the completion of this investigation.

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Cornell University.

ADSORPTION FROM SOLUTION BY ASH-FREE
ADSORBENT CHARCOAL. V

Adsorption from Buffer Solutions as a Means of determining the Isoelectric
Point for Charcoal^{1,2}

BY ELROY J. MILLER AND SELMA L. BANDEMER

Considerable attention has been given in recent years to the study of the buffer action of charcoal, chiefly on account of its significance for theories of buffer action in biological processes and because of the increasingly common use of charcoal for therapeutic purposes. A number of attempts have been made to determine the isoelectric point for charcoal. Two methods have been employed, the electrokinetic and adsorption from buffer solutions. By the first method the charcoal is held in the form of a membrane and the electro-osmotic flow of solution through the membrane is measured. The hydrogen ion concentration of the solution in which there is no movement of solution through the membrane under an applied difference of potential is taken as the isoelectric point. By the second method the charcoal is added to buffer solutions of various hydrogen ion concentrations and the hydrogen ion concentration of that solution in which there is no change in reaction is taken as the isoelectric point. This is essentially the method of Michaelis for the determination of the isoelectric point for amphoteric electrolytes. As might be expected from the discordant results reported for adsorption from solutions of electrolytes by charcoal the results of these studies likewise varied greatly and no definite hydrogen ion concentration has been accepted as the isoelectric point for charcoal. It was the object of this investigation to elucidate the causes of these discrepancies.

Previous Work

Briefly summarized, the results reported by a number of investigators are as follows: Bovie³ reported that charcoal possesses buffer properties. Rona and Michaelis⁴ reported that hydrogen and hydroxyl ions are equally adsorbed by blood charcoal. They based these conclusions on the fact that the charcoal adsorbed more acid from a mixture of acid and salt than from the same concentration of acid alone and likewise seemed to adsorb more alkali from an alkali-salt mixture than from the same concentration of alkali alone.

Löffler and Spiro⁵ found that blood charcoal has a neutralizing effect on buffer solutions. Acid buffer solutions were less acid and alkaline buffer

¹ Published as Journal Article No. 44 from the Chemical Laboratory of the Michigan Agricultural Experiment Station. Published by permission of the Director.

² Presented before the Colloid Division at the Detroit meeting of the American Chemical Society, September 5-10, 1927.

³ Bovie: *J. Med. Research*, 33, 295 (1915).

⁴ Rona and Michaelis: *Biochem. Z.*, 97, 85 (1919).

⁵ Löffler and Spiro: *Helv. Chim. Acta*, 2, 417 (1918).

solutions were less alkaline after treatment with the charcoal. An isoelectric point was found at approximately pH 8.5. They interpreted these results to mean that hydrogen ions were adsorbed from acid solutions and hydroxyl ions from alkaline solutions and considered it highly significant that a chemically inert substance, through adsorption processes, could cause the reaction of solutions to approach neutrality. They pointed out the possibility that adsorption by cells in the animal body might function in the same way. They also suggested that the favorable results obtained in the therapeutic use of charcoal in treatment of infectious diseases might be due, not only to the adsorption of bacteria and toxins, but to a reduction of the harmful acidity which accompanies these diseases.

Gyemant¹ working in Michaelis' laboratory found an isoelectric point for blood charcoal at pH 3.5 with H₂SO₄ and pH 3.95 with HCl by the electrokinetic method. Umetsu,² also in Michaelis' laboratory, found by the same method pH 3.0 as the isoelectric point for blood charcoal. Keeser,³ using Gyemant's apparatus found values of pH 3.5 and 4.0 for two brands of blood charcoal. For other charcoals values as high as pH 6.6 were obtained.

Kroetz⁴ found by adsorption from buffer solutions (phosphate) an isoelectric point for two samples of blood charcoal at pH 7.58. He claimed this to be the true isoelectric point for blood charcoal and that this method was not influenced by the impurities in the charcoal as was probably the case for the electrokinetic method. He claimed also that the "neutralization effect" reported by Löffler and Spiro held only for very acid and very alkaline solutions and not around the neutral point and, therefore, that the therapeutic use of charcoal depended upon the adsorption of toxic substances and not upon a regulation of the hydrogen ion concentration.

Bohn,⁵ from a study of adsorption from phosphate buffers, could assign no definite value as the isoelectric point for blood charcoal. His values varied from less than 4.8 to 6.8 and he attributed the variation, in part at least, to impurities in the charcoal. He concluded that the adsorption of hydrogen and hydroxyl ions took the form of typical adsorption isotherms.

From a review of these reports it is obvious that there is no definite pH that can be assigned as the isoelectric point for blood charcoal. It is evident also that the values obtained by the electrokinetic method do not agree with those obtained by the adsorption method. Furthermore, the results by either method alone are not consistent, except for the fact that as a general rule the very acid buffers became less acid and the very alkaline ones became less alkaline on treatment with charcoal.

Since adsorption from buffer solutions is essentially adsorption from acid-salt and alkali-salt mixtures it seemed likely that the information gained in

¹ Gyemant: *Kolloid-Z.*, 28, 103 (1921).

² Umetsu: *Biochem. Z.*, 135, 442 (1922).

³ Keeser: *Biochem. Z.*, 144, 536 (1924).

⁴ Kroetz: *Biochem. Z.*, 153, 173 (1924).

⁵ Bohn: *Biochem. Z.*, 178, 119 (1926).

the studies on adsorption from solutions of acids, bases, and salts, by pure charcoal might enable us to clear up and explain the causes of the discrepancies. This, indeed, proved to be the case.

In order to present the results of this investigation more clearly a brief summary of the more important and well established facts of adsorption by ash-free adsorbent charcoal that have a bearing on the present work will be given.

Activated sugar charcoal adsorbs acids but does not adsorb the inorganic bases.¹ It adsorbs certain acids, such as benzoic and salicylic very strongly, others such as succinic and tartaric moderately, and still others, such as formic, acetic, and the strong inorganic acids relatively slightly. The inorganic bases such as sodium, potassium, barium, calcium, and ammonium hydroxides are not adsorbed at all.

Glycine which is a constituent of some of the buffer mixtures is also not adsorbed.

Another property of activated sugar charcoal is that of hydrolytic adsorption. Such salts as sodium chloride, potassium sulphate, and sodium benzoate are hydrolytically adsorbed with the adsorption of acid and liberation of base. Salts of inorganic acids are exclusively hydrolytically adsorbed while those of more complex organic acids are partly hydrolytically and partly molecularly adsorbed.²

Still another fact which is of importance for the understanding of adsorption from the alkaline buffer solutions is that this hydrolytic adsorption takes place even in the presence of concentrations of alkali as high as hundredth normal. Thus, for example, potassium chloride was hydrolytically adsorbed in solutions of hundredth normal potassium hydroxide.

These properties of activated sugar charcoal were found to be common to all purified ash-free adsorbent charcoals whether of animal, vegetable, or carbohydrate origin.³

It was also established⁴ in the course of these researches that ordinarily blood charcoal contains adsorbed mineral acids and complex organic matter of an acid nature resulting from the incomplete decomposition of the organic material from which the charcoal had been prepared and that reaction with these acids was responsible for the supposed adsorption of bases by charcoal. When these impure charcoals were freed from inorganic matter and adsorbed acids they no longer had any effect on the bases.

From these facts it was expected a priori that:

1. Pure charcoal would decrease the acidity of the acid buffers through adsorption of acid.
2. The alkalinity of the less alkaline buffer would be increased through hydrolytic adsorption of salts with the liberation of alkali.

¹ Bartell and Miller: *J. Am. Chem. Soc.*, 45, 1106 (1923).

² Miller: *J. Am. Chem. Soc.*, 47, 1270 (1925).

³ Miller: *J. Phys. Chem.*, 30, 1031, 1162 (1926).

⁴ Miller: *J. Phys. Chem.*, 31, 1197 (1927).

3. Pure charcoal, unlike the impure charcoals, would not decrease the alkalinity of the more alkaline buffers.
4. When pure charcoal carried adsorbed acid it would give the same general results as the unpurified blood charcoal.
5. Unpurified charcoal after ignition to drive off acids would no longer cause the alkaline buffers to become less alkaline.

These expectations were all realized experimentally.

Materials and Procedure

The charcoals used in this investigation were blood charcoal, purified blood charcoal, purified wood charcoal, and activated sugar charcoal. The blood charcoal was a high grade material supplied for laboratory use. It had a high activity but carried nearly eight percent of inorganic matter and a considerable quantity of adsorbed acid and undecomposed organic matter. The purified blood and wood charcoals and the activated sugar charcoal were prepared according to methods previously described.¹ They contained at the most a few hundredths of a percent of ash and were free from adsorbed acids.

The buffer solutions were Sørensen's standards, prepared according to the directions of Clark.² One gram and five gram samples of freshly ignited charcoal were added to 30 cc. of buffer solutions. The flasks containing the suspension were evacuated to remove adsorbed gases from the charcoal and insure thorough contact of solution with the charcoal. The suspensions were shaken frequently during the course of one hour and then filtered through a disc of ash-free filter paper in a Gooch crucible.

Estimation of the hydrogen ion concentrations of the solutions before and after treatment with the charcoal was done colorimetrically.

Results with Blood Charcoal (not purified)

In order to determine whether the anomalous results reported by previous investigators could be reproduced, a number of buffer solutions were treated with unpurified blood charcoal. The results are presented in Table I. It will be observed first of all, that the acid buffers were less acid and the more alkaline buffers were, as a rule, less alkaline after treatment with the charcoal. There was no change, however, in the borate-NaOH buffers and in some of the borate-HCl buffers. As will be seen later, the reason for this is that the solutions are so highly buffered in these ranges that the addition or removal of a large amount of acid or alkali is necessary in order to produce a small change in the hydrogen ion concentration. Furthermore, as will be shown later, there were two counteracting factors operating which tended to prevent a large change in reaction. The active carbon adsorbed acid hydrolytically, liberating hydroxyl ions and making the solution more alkaline, while the adsorbed acid and acid organic matter in the charcoal reacted with the hydroxides and decreased the alkalinity. When the acids were removed from the impure

¹ Bartell and Miller: *J. Am. Chem. Soc.*, **44**, 1866 (1922); Miller: *J. Phys. Chem.*, **30** 1031 (1926).

² Clark: "The Determination of Hydrogen Ions," second edition p. 107.

TABLE I

Adsorption from Buffer Solutions by Blood Charcoal (not purified)

| Buffer | 1 gram charcoal pH | | 5 grams charcoal pH | |
|-------------------------|-----------------------|-------|------------------------|-------|
| | Before | After | Before | After |
| Glycine + HCl | 1.2 | 1.2 | 1.2 | 1.8 |
| | 1.9 | 2.2 | 1.9 | 3.0 |
| | 3.7 | 4.8 | 3.7 | 5.4 |
| Glycine + NaOH | 8.5 | 8.0 | 8.5 | 7.2 |
| | 8.8 | 8.5 | 8.8 | 7.5 |
| | 9.3 | 8.9 | 9.3 | 8.3 |
| Citrate + HCl | 1.2 | 1.2 | 1.2 | 2.0 |
| | 3.0 | 4.0 | 3.0 | 4.9 |
| | 4.9 | 5.4 | 4.9 | 5.8 |
| Citrate + NaOH | 5.0 | 5.5 | 5.0 | 5.8 |
| | 6.0 | 6.2 | 6.0 | 6.7 |
| | 6.7 | 6.9 | 6.7 | 7.2 |
| Borate + HCl | 7.6 | 7.4 | 7.6 | 7.0 |
| | 8.7 | 8.7 | 8.7 | 8.7 |
| | 9.2 | 9.2 | 9.2 | 9.2 |
| Borate + NaOH | 9.3 | 9.3 | 9.3 | 9.3 |
| | 9.5 | 9.5 | 9.5 | 9.5 |
| | 9.6 | 9.6 | 9.6 | 9.6 |
| Sørensen's phosphate | 5.3 | 5.5 | 6.6 | 6.0 |
| | 6.6 | 6.6 | 6.6 | 6.6 |
| | 8.0 | 7.8 | 8.0 | 7.6 |

charcoal the second factor was no longer operative and an increase in alkalinity of the buffer solution was actually observed. (See Table VII). When the amount of acid on the charcoal was increased the second factor predominated and a decrease in alkalinity took place (See Tables IV, V, VI).

Results with Purified Blood Charcoal

Buffer solutions were next treated with purified blood charcoal which, as previously stated, was free from ash, adsorbed inorganic acids, and acid organic matter. The results shown in Table II present a picture radically differ-

TABLE II
Adsorption from Buffer Solutions by Purified Blood Charcoal

| Buffer | 1 gram charcoal pH | | 5 grams charcoal pH | |
|-------------------------|-----------------------|-------|------------------------|-------|
| | Before | After | Before | After |
| Glycine + HCl | 1.2 | 1.6 | 1.2 | 1.9 |
| | 1.9 | 2.5 | 1.9 | 3.0 |
| | 3.7 | 7.0 | 3.7 | 8.6 |
| Glycine + NaOH | 8.4 | 8.6 | 8.4 | 8.8 |
| | 8.8 | 8.8 | 8.8 | 9.1 |
| | 9.2 | 9.2 | 9.2 | 9.3 |
| | 9.6 | 9.6 | 9.6 | 9.7 |
| | 9.9 | 9.9 | 9.9 | 10.1 |
| | 10.3 | 10.3 | 10.9 | 11.3 |
| | 10.9 | 10.9 | 11.1 | 12.2 |
| | 11.3 | 11.3 | 11.3 | 12.4 |
| | 11.9 | 11.9 | 11.9 | 12.2 |
| | 12.2 | 12.2 | 12.2 | 12.4 |
| | | 12.6 | 12.6 | |
| Citrate + HCl | 1.2 | 1.2 | 1.2 | 2.1 |
| | 3.0 | 4.4 | 3.0 | 5.2 |
| | 4.9 | 5.2 | 4.9 | 5.8 |
| Citrate + NaOH | 5.0 | 5.5 | 5.0 | 6.2 |
| | 6.0 | 6.6 | 6.0 | 7.8 |
| | 6.7 | 7.6 | 6.7 | 9.3 |
| Borate + HCl | 7.6 | 8.4 | 7.6 | 8.6 |
| | 8.7 | 9.0 | 8.7 | 9.1 |
| | 9.2 | 9.3 | 9.2 | 9.6 |
| Borate + NaOH | 9.3 | 9.3 | 9.3 | 9.6 |
| | 9.5 | 9.5 | 9.4 | 9.8 |
| | 9.6 | 9.6 | 9.6 | 10.0 |
| | 9.9 | 9.9 | 9.9 | 10.4 |
| | 10.9 | 10.9 | 10.9 | 11.4 |
| | 12.1 | 12.1 | 12.1 | 12.1 |
| Sørensen's phosphate | 5.3 | 6.2 | 5.3 | 6.8 |
| | 6.6 | 6.7 | 6.6 | 7.2 |
| | 8.0 | 9.2 | 8.0 | 9.2 |

ent from the one obtained with the unpurified material. In all cases the acid buffers were less acid due to adsorption of acid by the charcoal. On the other hand, in no case did an alkaline solution become less alkaline but, on the contrary, an increase in alkalinity was usually observed. This increase in alkalinity

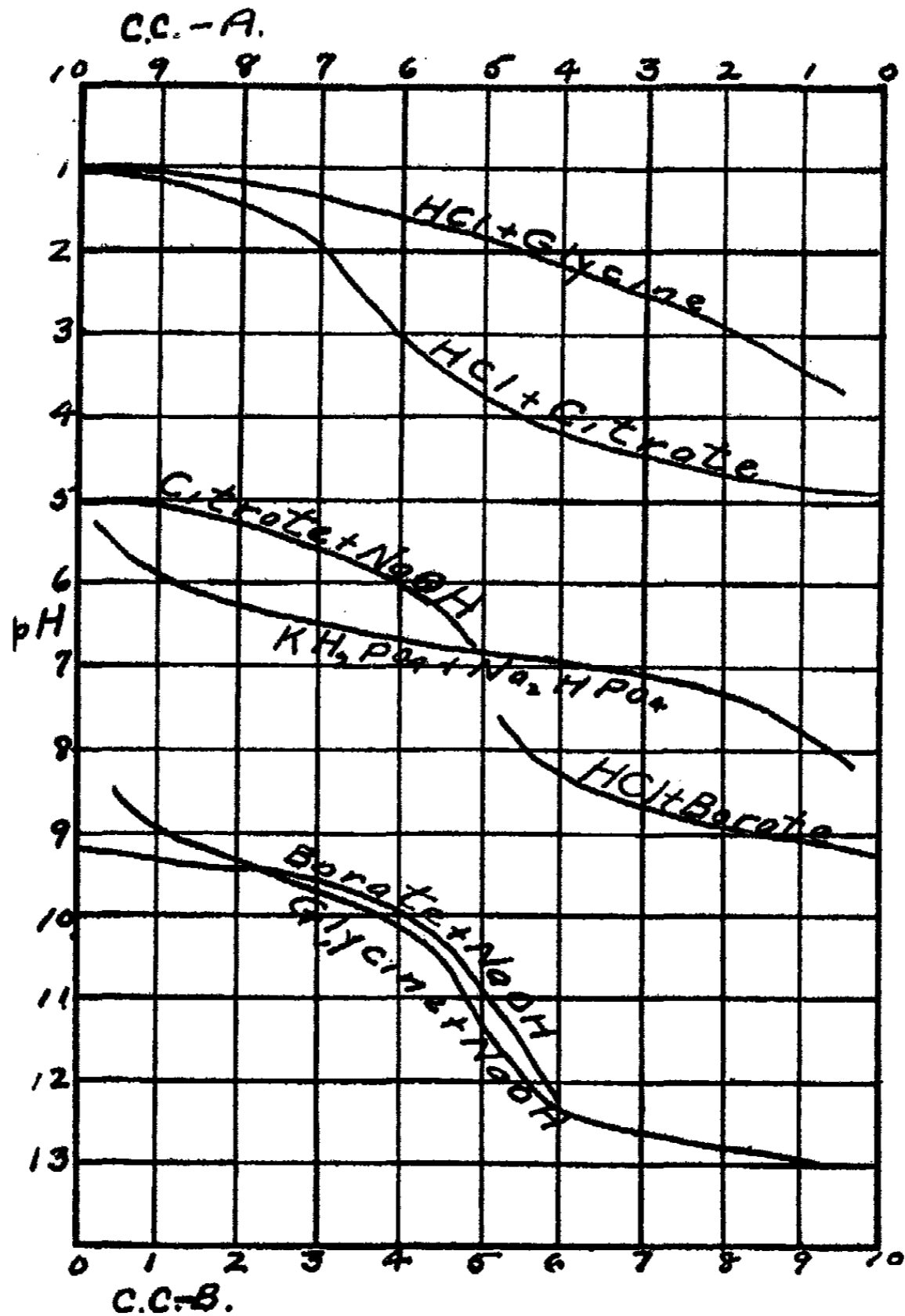


FIG. 1
Sørensen's Standard Mixtures
Mixtures of A parts of acid constituent and B parts of basic constituent.

ity was due to hydrolytic adsorption of the salts with the liberation of alkali. In those cases where no increase in alkalinity is indicated the reason is to be found in the fact that the changes were too small to be detected colorimetrically as, for example, in the results with one gram of charcoal on the glycine-NaOH buffers. When five grams of charcoal was used, easily detected

changes occurred. The changes in pH were greatest in those ranges where the buffering capacity was lowest; i.e., where the liberation of a small amount of alkali produces a large change in the pH value. These regions are indicated by the steep portions of the curves in Fig. 1. (For data on the actual amounts of alkali or acid necessary to produce these changes see tables given by Clark¹). Thus with five grams of charcoal and the glycine-NaOH buffers the greatest changes in pH were observed in the weakly buffered solutions ranging from pH 9.9 to 11.9 which corresponds to the steep part of the curve. On either side of this range smaller changes were observed.

TABLE III
Adsorption from Buffer Solutions by Purified Norit
and Activated Sugar Charcoal

| Buffer | 1 gram Norit pH | | 5 grams sugar charcoal pH | |
|-------------------------|--------------------|-------|------------------------------|-------|
| | Before | After | Before | After |
| Glycine + HCl | 1.2 | 1.2 | 1.2 | 1.3 |
| | 1.9 | 2.2 | 1.9 | 2.8 |
| | 3.7 | 5.2 | 3.7 | 8.2 |
| Glycine + NaOH | 8.5 | 8.5 | 8.5 | 8.5+ |
| | 8.8 | 8.8 | 8.8 | 8.8 |
| | 9.3 | 9.3 | 9.3 | 9.3 |
| Citrate + HCl | 1.2 | 1.2+ | 1.2 | 1.4 |
| | 3.0 | 4.0 | 3.0 | 4.7 |
| | 4.9 | 5.2 | 4.9 | 5.4 |
| Citrate + NaOH | 5.0 | 5.2 | 5.0 | 5.4 |
| | 6.0 | 6.4 | 6.0 | 7.0 |
| | 6.7 | 7.7 | 6.7 | 9.2 |
| Borate + HCl | 7.6 | 7.9 | 7.6 | 8.3 |
| | 8.7 | 8.8 | 8.7 | 9.0 |
| | 9.2 | 9.3 | 9.2 | 9.4 |
| Borate + NaOH | 9.3 | 9.4 | 9.3 | 9.4 |
| | 9.5 | 9.5+ | 9.5 | 9.5+ |
| | 9.6 | 9.6+ | 9.6 | 9.6+ |
| Sørensen's phosphate | 5.3 | 5.8 | 5.3 | 6.2 |
| | 6.6 | 6.8 | 6.6 | 6.8 |
| | 8.0 | 8.5 | 8.0 | 9.2 |

¹ Clark: "The Determination of Hydrogen Ions," second edition p. 111.

Similarly for the borate-NaOH mixtures, one gram of charcoal was not sufficient to produce marked changes in pH but with five grams the changes were easily measured and were greatest in the ranges corresponding to the steep part of the curve.

It should be pointed out that in the glycine-NaOH buffer neither the glycine nor sodium hydroxide is adsorbed by pure charcoal and the increase in alkalinity of these solutions is due to NaOH set free by hydrolytic adsorption of the tenth normal sodium chloride present in the buffer mixture.

Similar changes were observed with other buffer systems and without going into further detail it may be stated that in all cases the results were consistent with and readily explainable on the basis of the known facts of adsorption by ash-free and acid-free adsorbent charcoals.

TABLE IV

Adsorption from Buffer Solutions by Ash-Free Blood Charcoal carrying Adsorbed Acids

| Buffer | 1 gram charcoal + 0.83 millimol stearic acid pH | | 1 gram charcoal + 0.20 millimol stearic acid pH | |
|-------------------------|-------------------------------------------------------|-------|-------------------------------------------------------|-------|
| | Before | After | Before | After |
| Glycine + HCl | 3.7 | 4.2 | 3.7 | 4.9 |
| Glycine + NaOH | 8.5 | 7.2 | 8.5 | 7.8 |
| | 9.3 | 8.7 | 9.3 | 9.0 |
| Citrate + HCl | 3.0 | 3.4 | | |
| | 4.9 | 5.1 | | |
| Citrate + NaOH | 5.0 | 5.1 | | |
| | 6.0 | 6.1 | 6.0 | 6.1 |
| | 6.7 | 6.6 | | |
| Borate + HCl | 6.6 | 5.7 | | |
| | 8.7 | 8.5 | | |
| | 9.2 | 9.0 | | |
| Borate + NaOH | 9.3 | 9.1 | | |
| | 9.6 | 9.4 | | |
| Sørensen's phosphate | 6.2 | 6.3 | | |
| | 6.4 | 6.5 | 6.4 | 6.6 |
| | 6.6 | 6.6 | 6.6 | 6.7 |
| | 6.8 | 6.7 | 6.8 | 6.8 |
| | 7.0 | 6.8 | 7.0 | 7.0 |
| | | 7.2 | 7.1 | |

Results with Purified Norit and Activated Sugar Charcoal

In Table III are results obtained when purified Norit and activated sugar charcoal were used in place of the purified blood charcoal. These results show that here again, as in the previous adsorption studies, the pure charcoals, regardless of origin, all exhibited the same behavior. The acid buffers became less acid and the alkaline buffers either did not change at all or became more alkaline, depending upon the buffering capacity of the solution, the amount of charcoal used, and its activity.

Results with Purified Charcoal carrying Adsorbed Acids

If the neutralizing effect of the impure charcoals on the alkaline buffer solutions is due to the presence of acid impurities then it should follow that the pure charcoals carrying adsorbed acid should give the same results as the impure charcoals. This, too, was found to be true. Varying amounts of acids of different types were added to purified blood charcoal. The amount of acid added to the charcoals was sufficiently small so that it was irreversibly adsorbed and could not be detected by extraction with water or the solvent from which it had been adsorbed.

From the data in Tables IV and V it will be seen that charcoal carrying adsorbed stearic acid or methyl red acid, (*o*-carboxy benzene azo dimethyl aniline), like the impure charcoal, was still able to reduce the acidity of the acid buffers and likewise reduced the alkalinity of the more alkaline buffers.

TABLE V

Adsorption from Buffer Solutions by Ash-Free Blood Charcoal carrying Adsorbed Acids

| Buffer | 1 gram charcoal + 0.25 millimol methyl red acid pH | |
|----------------------|----------------------------------------------------------|-------|
| | Before | After |
| Glycine + NaOH | 8.5 | 9.2 |
| | 8.8 | 8.6 |
| | 9.3 | 9.0 |
| Borate + HCl | 6.6 | 7.2 |
| | 8.3 | 8.4 |
| | 8.7 | 8.7 |
| | 9.2 | 9.2— |
| Borate + NaOH | 9.3 | 9.2 |
| | 9.6 | 9.4 |
| Sørensen's phosphate | 5.3 | 5.4 |
| | 6.6 | 6.7 |
| | 8.0 | 8.0— |

These complex water-insoluble organic acids were used to simulate the complex acid organic matter in the impure charcoals. The impure blood charcoals carry also inorganic acids such as hydrochloric and sulfuric, with which they have been treated in attempts at purification. Experiments were, therefore, carried out using charcoal carrying adsorbed hydrochloric and benzoic acids. The results (Table VI) again indicate the similarity of behavior of these charcoals and the unpurified materials in that the more alkaline buffers become less alkaline on treatment with the charcoal, the magnitude

TABLE VI
Adsorption from Buffer Solutions by Ash-Free Blood Charcoal carrying Adsorbed Acids

| Buffer | 5 grams charcoal + 0.5 millimol HCl pH | | 5 grams charcoal + 4 millimols benzoic acid pH | |
|-------------------------|----------------------------------------------|-------|------------------------------------------------------|-------|
| | Before | After | Before | After |
| Glycine + NaOH | 8.3 | 8.0 | | |
| | 8.6 | 8.5 | 8.6 | 6.6 |
| | 9.3 | 8.9 | 9.3 | 6.9 |
| Citrate + NaOH | 5.0 | 5.5 | | |
| | 6.0 | 7.2 | 6.0 | 6.2 |
| | 6.7 | 8.2 | 6.7 | 6.4 |
| Borate + NaOH | 9.3 | 9.3 | | |
| | 9.5 | 9.5 | 9.5 | 8.7 |
| | 9.6 | 9.6 | 9.5 | 8.8 |
| Sørensen's phosphate | 5.3 | 5.6 | | |
| | 6.6 | 6.7 | 6.6 | 6.4 |
| | 8.0 | 8.0 | 8.0 | 7.0 |

of the change depending upon the amount of acid on the charcoal and also upon the type of acid on the charcoal. Thus, for illustration, with adsorbed hydrochloric acid on the charcoal the alkali is neutralized with the formation of sodium chloride which is not adsorbed and remains in solution. With the complex organic acids neutralization takes place and part of the salt formed is held adsorbed and part remains in solution. In either case, of course, the alkalinity of the solution is decreased.

It should not be inferred that all the adsorbed acid on the charcoal reacts with the alkali in solution. Such is not the case. How far or to what extent the reaction takes place depends upon the amount of acid on the charcoal, the concentration of alkali in solution, the concentration of salt, and other factors.¹

¹ Miller: J. Am. Chem. Soc., 47, 1270 (1925).

Results with Ignited Blood Charcoal

Further evidence that the unpurified blood charcoal contained acid impurities is found in the fact that after ignition at a temperature of 1000° the charcoal gave an alkaline water extract and no longer had a neutralizing effect on the alkaline buffers. Like the purified charcoal it decreased the acidity of the acid buffers and increased the alkalinity of the alkaline ones. The data for the ignited blood charcoal are given in Table VII.

TABLE VII
Adsorption from Buffer Solutions by Unpurified Blood Charcoal
heated at 1050°

| Buffer | 1 gram charcoal pH | |
|-------------------------|-----------------------|-------|
| | Before | After |
| Glycine + NaOH | 9.5 | 9.5+ |
| | 9.9 | 10.2 |
| | 10.3 | 10.5 |
| | 10.9 | 11.2 |
| | 11.1 | 11.3 |
| | 11.3 | 11.4 |
| | 11.9 | 12.0 |
| | 12.2 | 12.2+ |
| | 12.4 | 12.4 |
| | Borate + NaOH | 9.6 |
| 9.9 | | 10.1 |
| 10.9 | | 11.0+ |
| 12.1 | | 12.1 |
| Sørensen's phosphate | 5.3 | 6.6 |
| | 6.6 | 7.0 |
| | 8.0 | 10.0 |

Discussion

From these results and their underlying causes it is certain that the method of adsorption from buffer solutions cannot be used for the determination of the isoelectric point of charcoal. In the first place, the method was based on conclusions that were founded on erroneous experimental evidence, namely that charcoal adsorbs both acids and bases and that hydrogen and hydroxyl ions are about equally adsorbed.¹ It has been abundantly shown that this "ampholytoid"² behavior is not a specific property of charcoal and that the supposed adsorption of bases is in reality not adsorption but neutralization by acid impurities in the charcoal.³ The results presented in this paper are in keeping with and support the earlier findings.

¹ Rona and Michaelis: *Biochem. Z.*, 97, 85 (1919).

² Michaelis: "Hydrogen Ion Concentration," 239, 242.

³ Bartell and Miller: *J. Am. Chem. Soc.*, 45, 1106 (1923); Miller: 47, 1270 (1925); *J. Phys. Chem.*, 30, 1162 (1926); 31, 1197 (1927).

In the second place, the results by this method do not agree with and apparently have no relation to the isoelectric point as determined by electrokinetic methods. According to this method pure charcoal would have no isoelectric point and each impure charcoal would have a different point for each buffer and these points would vary depending upon the quantity of charcoal used and other factors.

Svedberg¹ has pointed out that it has never been proved that the electrokinetic isoelectric point and the Michaelis isoelectric point are the same. He also states that the application of the theory to the colloidal particle must be done with caution, for the theory is based on the assumption that it is only the hydrogen and hydroxyl ions that are involved whereas it has been shown from cataphoresis studies that other ions do have an effect. Kruyt and Tendeloo² recently have found additional evidence that ions other than H^+ and OH^- determine the isoelectric point.

A consideration of the facts now at hand for charcoal reveals conclusive evidence that the two methods do not give the same results. From an inspection of the data in the literature on the determination of the isoelectric point for charcoal by the electrokinetic method it seems fairly certain that the point at which there is no movement in an electric field is on the acid side. In general, the smallest electrokinetic effects were observed in solutions of acids. The charge on the charcoal was sometimes positive, sometimes negative, and in some cases zero.

In solutions of the alkalis the charcoal was always negatively charged and the electrokinetic effects were greatest. It is interesting and significant that the greatest electrokinetic effects take place in solutions of the alkalis which are not adsorbed by charcoal while the lesser effects occur in solutions of acids which are strongly adsorbed. Furthermore, inactive sugar charcoal which adsorbs neither acids nor bases gives greater electroendosmotic effects than the activated sugar charcoal with a high adsorption capacity.

These facts seem to afford additional evidence that for colloidal particles the Michaelis isoelectric point cannot be the same as the electrokinetic isoelectric point.

Summary and Conclusions

1. Adsorption from buffer solutions by charcoal has been studied.
2. Adsorption from buffer solutions by charcoals produces changes in reaction which are in keeping with the established facts of adsorption by pure adsorbent charcoals.
3. Pure charcoal decreases the acidity of acid buffer mixtures through its ability to adsorb acids.
4. Pure charcoal increases the alkalinity of the less alkaline buffers through hydrolytic adsorption of acid from salts with the liberation of alkali.
5. Pure charcoal does not reduce the alkalinity of the highly alkaline buffers because it does not adsorb the inorganic hydroxides.

¹ Svedberg: "Colloid Chemistry," 199.

² Kruyt and Tendeloo: *J. Phys. Chem.*, 29, 1303 (1925).

6. Pure charcoal carrying adsorbed acids reduces the alkalinity of the more alkaline buffers by neutralization.
7. Unpurified blood charcoal, as reported by previous investigators, reduces the alkalinity of the more alkaline buffers. From our work it is certain that this is due to the presence of acid impurities in the charcoal.
8. Unpurified blood charcoal after ignition to drive off or decompose the acid impurities no longer reduces the alkalinity of the more alkaline buffers.
9. The results of this investigation show that the method of adsorption from buffer solutions cannot be used for the determination of the isoelectric points for charcoals.
10. It is necessary to revise the explanations of biological phenomena which are based on erroneous data obtained with impure charcoal.

*East Lansing,
Michigan.*

THE ELECTROCHEMICAL BEHAVIOUR
OF SILICATE GLASSES. IV*
SOLID ELECTROLYTIC DEPOSITS**

BY M. J. MULLIGAN, J. B. FERGUSON AND J. W. REBBECK

When a tube of soda-lime glass was electrolysed first with mercury as anode for a long time and then with mercury as cathode for a shorter time, the tube became brownish in colour.¹ Microscopic examination showed that the colour was due to a formation of a brownish deposit in the glass near the mercury-glass interface. In new glass² this deposit appeared initially as very minute spots just visible at a magnification of 100 diameters.

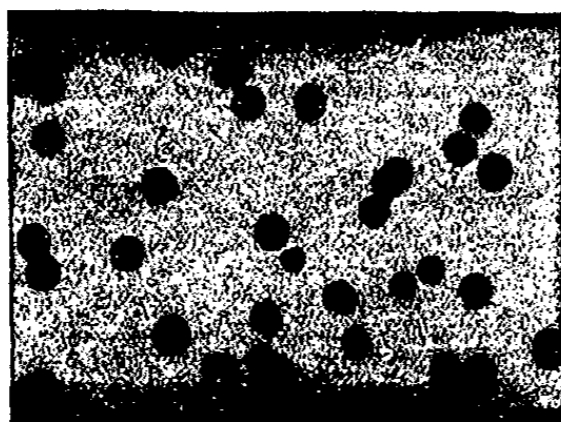


Plate 1

Brown Deposits, ($\times 100$).

A new soda-lime glass tube was electrolysed for 15.25 hours at 100°C with 110 volts, mercury anode, and then with mercury cathode for 57 minutes.



Plate 2

Brown Deposits, ($\times 100$).

A similar tube was electrolysed for 12 hours at 100°C with 110 volts, mercury anode, and then mercury cathode for 3.66 hours.

On further electrolysis with mercury cathode the spots often formed rings and these later became patches which eventually covered most of the glass. They were not more than one or two μ below the glass surface and probably less than this.³ Photographs of these are shown in Plates I and II.

Deposits were also obtained with well-annealed glass under the same electrical treatment but consisted of fine spots which even initially were uni-

* Contribution from the Department of Chemistry, University of Toronto.

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¹ The sample tubes were similar to those used by Rebeck and Ferguson: *J. Am. Chem. Soc.*, 46, 1991 (1924) and a similar experimental procedure was employed. The colour was first noted by Rebeck.

² New glass is used to signify glass which has not been subjected to any especial thermal, electrical or other treatment. References for glass compositions may be found in Paper III, *J. Phys. Chem.* 32, 779 (1928).

³ Ferguson and Ellis: *Trans. Roy. Soc. Canada*, (3) 19, 34 (1925). Abstract only.

formly spread over the glass. Partially annealed glass yielded deposits intermediate in type between these extremes.¹

When silver was electrolysed from a suitable anode liquid into the soda-lime glass² and the glass then used with the silver-containing glass next to the mercury electrode, deposits were formed which were quite different in character. With new glass they were definitely crystalline and photographs of these are given in Plates III and IV.³ With well-annealed glass the deposits were so fine grained that no details could be made out with the microscope. The lighter ones gave the tubes a greenish appearance in transmitted light and the heavy deposits rendered the glass opaque much like an over-exposed developed photographic plate.

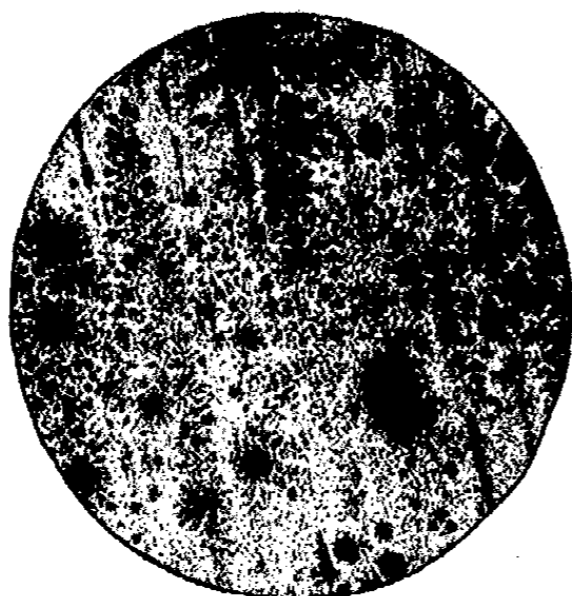


Plate 3

Crystalline Deposits, ($\times 30$).

Silver was electrolysed into new soda-lime glass from a 0.02 N silver nitrate aqueous solution at 100°C with 110 volts for 15.25 hours. The solution was replaced with mercury and the electrolysis continued for 17.8 hours with mercury anode and then for 3.5 hours with mercury cathode.

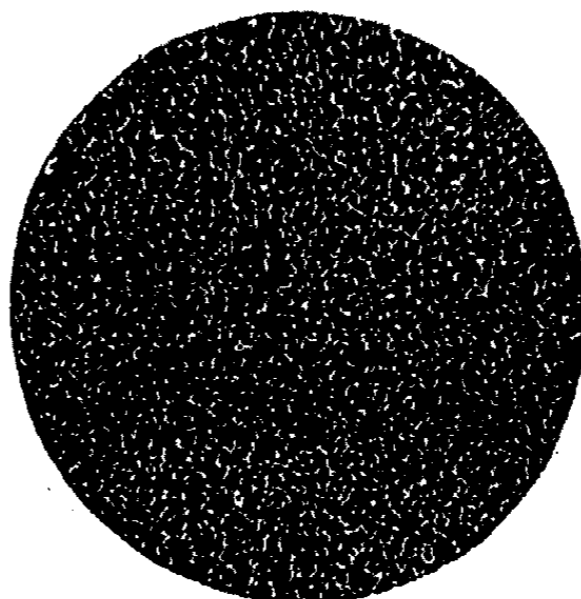


Plate 4

Crystalline Deposits, ($\times 30$).

Silver was electrolysed from a silver nitrate melt at 287°C for 5 minutes with 110 volts into new soda-lime glass. The melt was replaced with mercury and the electrolysis continued with this as anode for 3.6 hours at 100°C using 110 volts, then as cathode for 29.75 hours. The tube was opaque to the naked eye.

The brownish deposits were formed in soda-lime glass using mercury first as anode and then as cathode with 110 volts across the tube wall at temperatures from 74 to 300°C, and under similar conditions at 100°C with Schott glasses 59^{III}, 3818^{III}, 1003^{III} and 16^{III}. When the mercury was replaced by molten tin and the experiment carried out at 250°C using soda-lime glass, the deposit was less definite and still less so when graphite was used.

The crystalline deposits were obtained with soda-lime glass containing silver using mercury as the electrode with 110 volts at temperatures from 100°

¹ Annealed means held for many hours at temperatures between 350 and 400°C while exposed to the laboratory air.

² Schulse: *Ann. Physik*, 40, 335 (1913); Mulligan: *Trans. Roy. Soc. Canada*, (3) 19, 35 (1925).

³ We are indebted to Mr. S. F. Kelly for assistance with these photographs. A plate similar to III was published by Ferguson: *Can. Chem. Met.*, 10, 131 (1926).

to 300°C and at the higher temperatures with molten tin and graphite as electrodes. Beautiful crystalline rosettes, three millimeters in diameter, were obtained with the latter electrodes. Deposits were also obtained with the following Schott glasses into which silver had first been electrolysed: type 59^{III} using a molten tin electrode at 250°C; type 59^{III} using a carbon electrode at 290°C; type 59^{III} using a mercury electrode at 100°C; types 1447^{III}, 1003^{III} and 2814^{III} using mercury at 260°C. These deposits were initially bright and silvery in appearance but in some cases, especially at the high temperatures, after a prolonged electrolysis a graphitic type of product was formed in addition.

Experiments were carried out with new soda-lime glass in which the first electrolysis was with mercury as anode; the mercury was then replaced with an aqueous solution of sodium chloride and the electrolysis continued with this as the cathode liquid. No appreciable deposit formed but a faint indication of one which disappeared on further electrolysis. When silver-containing glass was used, a crystalline deposit was obtained and this was similar in appearance to that produced when the mercury was the final cathode liquid.¹

When silver was electrolysed into new glass tubes from aqueous solutions of silver nitrate, these tubes gave deposits which were mainly confined to the freshly blown portions such as the shoulder and end. However, the deposits were found on all parts of the tubes when melts of silver nitrate were used or when annealed glass was electrolysed with the aqueous solution. Rebbeck and Ferguson noted that little gas was evolved from the freshly blown portions of tubes in ordinary experiments. We have also reported in Part III that gas and an interfacial deposit were obtained with glass into which the silver had been introduced from an aqueous solution but only the deposit in the cases in which annealed glass or a silver nitrate melt was used. The results of these diverse experiments are in substantial agreement with each other and support the hypothesis, that the glass surface is not uniform in its permeability to the various ions, which has been discussed in Part III.

If the brown rings were made at 100°C using mercury as the electrode and the mercury then made anode they would disappear but left a mark in the glass and on making the mercury again cathode, as nearly as one could tell, reappeared in the same places. Well-developed brown deposits would not disappear in this fashion. In similar experiments with crystalline deposits, these did not disappear but in some cases seemed to get thinner.

Chemical Nature of the Deposits

(a) *Brown Deposits*: Schulze has found that mercury can be quantitatively electrolysed into glass at high temperatures² and we have noted a marked increase in weight with a soda-lime glass sample when it was electrolysed at 308°C with 110 volts using a mercury anode. At 100°C no such weight in-

¹ The nature of the electrode material next the glass surface under investigation is usually the only one given. At and below 100°C the other electrode material was a 5% by weight aqueous solution of sodium hydroxide unless otherwise stated. This solution was covered with paraffin to prevent evaporation and electrical leakage.

² Schulze: *Ann. Physik*, 37, 435 (1912).

crease could be observed after a reasonable time. After such an electrolysis at 308° the anode side of the glass sample gave interference colours in reflected light and on heating the glass to a high temperature a play of colours similar to those noted by Schulze. After an electrolysis at 100°C for many hours similar interference colours could be seen but in this case violet and green predominated. The similarity in the electrical and chemical behaviour of these glasses led us to believe that mercury also enters the glass at the lower temperature but in too small quantities to be readily detected. From the interference colours the layers of mercury-containing glass would range from 0.4 to 2 μ in the various experiments in which the electrolysis was either long continued at the low temperature or several hours at the higher temperature.

On the assumption that a layer of mercury-containing glass formed in all cases in which mercury was used as the anode, the brown deposit must result from a reaction at the junction of this layer with the unchanged glass. The common constituents in our soda-lime glass and Schott glass 59^{III} are Na₂O and SiO₂. These and mercury would appear therefore to be the chemicals which might be involved since the deposits obtained with these glasses seemed identical. In the original glass the current is practically all carried by the sodium¹ and this might react with the mercury-containing glass to free silicon.

The deposits were not appreciably affected by treating the tubes with any reagent which did not etch the glass. The outer protecting glass layer could be removed with cold hydrofluoric acid and the deposit obtained in the form of a fine material much like lamp black, which was very difficult to handle and was certainly not pure. It was insoluble in all the common acids or mixtures of these with the exception of a mixture of nitric and hydrofluoric acids. Some samples dissolved in strong alkali. If adhering materials did not vitiate the result, the deposits were of the same density as the glass, rising and sinking in the same solutions.

These direct observations were supplemented by observing the deposits which formed when the mercury-containing glass was placed in contact with sodium amalgam. Such treatment even at room temperature gave dark deposits with soda-lime glass which had been electrolysed with a mercury anode at any temperature between 74 and 300°C. Similar deposits were not formed with new glass even at 275°C, nor with Pyrex or silica glass at 100°C, nor with new glass into which sodium had been electrolysed from a sodium nitrate melt, but were formed with the mercury-glass anode layers prepared on glasses 59^{III}, 1003^{III}, 1447^{III} and 2814^{III}. The amalgam deposits had the same chemical properties as the electrolytic ones and the evidence as a whole seemed to indicate that the latter were silicon.

The brown deposits obtained with tin and carbon electrodes were not definite enough to warrant any chemical investigation and similar ill-defined products were obtained with the amalgam treatment. Schulze reports that tin is a soluble anode and carbon insoluble but his results with tin are not conclusive and it may also be insoluble.

¹ Rebbeck and Ferguson: loc. cit.; Mulligan, Ferguson and Rebbeck: *J. Phys. Chem.*, **32**, 779 (1928).

(b) *Silvery Deposits*: The formation of these deposits with various original glasses and with the four types of electrode materials, and their general appearance, suggested that they were probably silver. They were also protected by an outer film of glass and generally were not affected by filling the tubes with liquids which did not etch the glass film. In a few cases nitric acid dissolved minute parts of the crystalline masses but stopped at this stage. On dissolving the outer glass film with cold hydrofluoric acid and washing with distilled water a solid concentrate was obtained which was suitable for further work. This treatment was found to remove the silver present in the silver-containing glass. The concentrate from a heavy deposit was treated with nitric acid. The silvery material dissolved and the silver in the solution was determined as the chloride. It amounted to more than 50% of the concentrate. Magnesium, calcium and silicon were also present. The magnesium and calcium probably came from the original glass. The silicon may in part have had a similar origin or may have been derived from some of the graphitic material which had also been formed.

(c) *Graphitic Deposits*: These formed when the final electrolysis was continued for a long time with glass containing silver and were especially noticeable at the high temperatures. Their behaviour with acids was the same as that of the brown deposits but they did not appear to be readily attacked by alkali. A similar type of material was formed when soda-lime glass into which silver had been electrolysed either from melts or aqueous solutions was treated with sodium amalgam at 275°C. The chemistry of silicon is none too well understood, there being several crystalline modifications, but it seems probable that the graphitic products are silicon formed by the reduction of the silicates by sodium.

Theory of Deposit Formation¹

When the direction of the current is reversed on a tube into which mercury has been electrolysed at high temperatures, according to Schulze, the mercury-containing glass film is punctured, the resistance falls and light is emitted as from sparks. The assumption that our anode glass layers are also punctured would explain the formation of the solid electrolytic deposits. The evidence favourable to this suggestion is as follows:

The protection afforded the silvery deposits by the outer glass film was not always complete and in certain cases minute parts of the deposits dissolved when nitric acid was placed in the tubes. These parts were always at the points from which the individual crystalline masses started to form. Dark spots may be noted in Plates I and II. The patches started at these spots which were not affected by washing with water but on treatment with nitric acid disappeared. The patches were then of uniform density and, although there was a faint indication that they had been attacked where the spot had been, it could not be definitely established.

¹ We wish to thank Professor T. L. Walker of the Dept. of Mineralogy and Professor J. C. McLennan of the Dept. of Physics and their respective colleagues for assistance in the preliminary study of these deposits.

When the final cathode liquid was an aqueous solution, no deposit was formed with new glass but with silver-containing glass the usual silvery deposit was obtained. This would seem to indicate that the deposits started from points which were in contact with the solutions and in the first case these prevented the reduction of the silicates to silicon.

At low temperatures, the glass surfaces were as smooth after deposit formation as before and no pitting could be seen nor could it be detected by means of a needle. The use of stains did not help but this was not surprising since the pits, if they existed, would have a depth of only one or two μ . Heavy deposits formed at high temperatures caused the glass surfaces to be roughened, but this could have been caused by a splitting of the outer glass film due to the accumulated deposit beneath it. In all cases the film appeared to be under strain and could be more readily crushed by a file than the original glass. In a very few cases actual holes were observed at the centres of heavy deposits.

The current fell rapidly when a tube was electrolysed at 250 to 300°C with 110 volts and mercury anode. An electric lamp in series with the tube soon became dim and ceased to light. On reversing the current, the lamp immediately became bright and remained so if a soluble anode such as sodium nitrate or silver nitrate were used as the other electrode material. The electrical phenomena appear to be similar to those described by Schulze although we saw no sparks.

The electrical behaviour at lower temperatures and different applied voltages will be discussed in detail in the next paper. A potential difference of 110 volts was applied to several tubes with mercury anode. When the current readings at 100°C had fallen to low values, the tubes were ready for further experimentation. If the mercury were made cathode and the applied voltage low, the current readings still fell to low values. At 60 to 80 volts, the readings instead of falling with time rose and the higher the voltage the more rapid the increase. At the same time the number of deposit spots also rapidly increased. These were observed from time to time under the microscope. Very few spots were obtained with from 20 to 40 volts at which the current readings, mercury cathode, were approximately the same as those obtained with mercury anode and the same applied voltages. When the tube with a mercury-containing glass film was electrolysed at 100°C with 110 volts for a few minutes with mercury cathode, the time was too short for the formation of a visible deposit. If the voltage were then reduced to 20 volts and the electrolysis then continued for a long time spots formed. These did not increase in number as the electrolysis continued but grew darker. The current reading was taken at 20 volts with mercury anode, the higher voltage then applied with mercury cathode for a few minutes, and readings again taken with mercury anode and 20 volts. In some cases the final reading was ten times the initial reading. When the higher voltage was again applied but with mercury anode a very short time was sufficient to restore the tube to its original highly resistant condition. The rapidity with which this was accomplished was such that one might question if this were compatible with a

theory of puncture. However, a similar phenomenon was noted by Schulze who had more direct evidence of puncturing in his work at the higher temperatures.

While the evidence points strongly to a puncturing as the causative factor in deposit formation, this suggestion cannot be accepted until an adequate explanation is given both of the puncturing and of the method by means of which this causes deposits to be produced.

The electrical measurements show that on making the mercury finally cathode and using sufficiently high voltages, the insulating property of the anode layer was rendered less effective as though at certain points good contacts were established between the electrode and the original glass. If instead of making the mercury finally cathode, it is removed after the layer is formed and replaced with aqueous solutions of silver nitrate, sodium nitrate, sodium chloride or sodium hydroxide and the electrolysis continued with these as *anode* liquids, the measurements at 100°C and various voltages were similar in character to those obtained with mercury cathode, increasing markedly at the higher voltages with the time of electrolysis. After one such experiment the solution was replaced by mercury and the electrolysis continued with this as cathode. A dark deposit formed in the usual manner so that the layer did not seem to have been etched away by the solution. Since similar electrical observations were made with the different solutions we assumed that they also did not dissolve the anode glass film. When the original mercury was replaced with an aqueous solution of mercuric chloride and the electrolysis carried out with this as cathode, the results were similar to those obtained with the other solutions. When the electrolysis was carried out with this solution as anode the readings at the higher voltages did not increase with time but decreased. The actual readings were much higher than those obtained with metallic mercury but otherwise the behaviour was similar. When aqueous solutions of sodium salts were used as anodes next to the mercury-containing glass, no deposit was observed. When aqueous solutions of silver nitrate were used as anodes in a similar way, the anode glass surface became covered with a fine deposit which gave the glass a milky appearance and this is all we can say about it. In certain experiments in which the anode glass surface had originally some surface defects, such as bubble holes, silver was deposited in these defects.

Attempts were also made to see the effect of using a sodium amalgam in place of the aqueous solutions but the amalgam attacked the surface layer so that the subsequent electrical measurements could not be interpreted.

The mass of evidence now available indicates that the conduction process with ordinary glass is always essentially electrolytic in character even at high voltages.¹ Schulze has also shown that the same is true for the mercury-containing anode layer. The nature of the conduction process in a layer formed with an insoluble anode is still in doubt but it seems reasonable to

¹ Schiller: *Ann. Physik*, 83, 137 (1927); Quittner: *Sitz. Akad. Wiss. Wien*, 136 IIa, 151 (1927); Rebbeck and Ferguson: *loc. cit.*

assume that it too is electrolytic although the number of carriers may be small and their migration velocity slight. Our observation of deposit formation with silver-containing glass and our electrical results in general certainly indicate no marked difference in this property even for layers formed with carbon.

On the assumption that the conduction in the anode glass layers is electrolytic in character, our experiments indicate that when rapidly moving ions like those of sodium or silver reach the anode layer, they penetrate it readily in spots, and the origin of these ions may be either aqueous solutions or the original glass. A number of methods by means of which this penetration may occur have been considered. One, based upon the setting up of local strains which operate in a plane parallel to the glass surface and which cause a rupture of the glass film, was the least objectionable of these. Our information is not sufficient at present to enable us to make a definite statement on this point.

Once a puncture has formed, a deposit may easily be built up. In the one case the sodium from the glass is set free at the edge of the puncture and there reacts with the anode layer to free silicon. More sodium is freed at the edge of this silicon which is a metallic conductor and this in turn forms more silicon and the deposit is built up. In the other case the silver does not react with the anode layer and a deposit of this metal is consequently formed.

An important deduction from our results and the discussion is that the dielectric strength of the anode layers is not an intrinsic property of these layers but is also a function of the nature of the ions which are entering them.

The silver deposit formed in glass defects when silver nitrate solutions were used as the anode liquids was not further investigated. Its formation may be related to the so-called electrostenolytic phenomenon.¹

In all cases in which this has been observed, the good-conducting electrolyte has been free to move and this property is an essential part of the explanation which has been given of such deposit formations. A similar movement of the electrolyte in a glass defect is not possible and to this extent our deposits differ from those usually designated as electrostenolytic products. The formation of the milky deposit may be due to the same factors that caused the silver deposits in the defects and would then indicate the presence of minute defects, i. e. punctures.

Glass Regeneration

Le Blanc and Kerschbaum² state that at their high temperatures a glass which had been electrolysed with a mercury anode could be brought back to its original condition by further electrolysis with the current reversed and sodium amalgam as the anode. Quittner has also presented some results obtained at high voltages and ordinary temperatures which point to a regeneration of a sodium deficient layer. We have likewise noted that on current reversal the current reading may in time attain a value nearly if not exactly

¹ Braun: *Wied. Ann.*, 42, 450 (1891); 44, 473 (1891); Coehn: *Z. physik. Chem.*, 25, 651 (1898); Holmes: *J. Am. Chem. Soc.*, 36, 784 (1914).

² LeBlanc and Kerschbaum: *Z. physik. Chem.*, 72, 468 (1910).

equal to the reading initially obtained with the original glass. This does not necessarily mean that the glass has been regenerated in a strictly chemical sense. The puncturing reported by Schulze and the deposits observed by us quite definitely indicate that in many cases strictly chemical regeneration does not take place.

Gas Reappearance

In the previous paper the slow reappearance of gas after it has been caused to disappear has been commented upon and the reason for this is now apparent. As most of the sodium is used up before it reaches the mercury, a long time is required before there is a sufficient supply at the mercury-glass interface to produce the gas.

In conclusion we wish to thank Professors T. L. Walker and J. C. McLennan and also Dr. Horovitz for the assistance which they afforded us in this work.

Summary

1. Solid electrolytic deposits may be formed in glass near the surface. Those observed consisted mainly of silicon or silver depending on the materials used in the experiments.
2. The important factor in deposit formation appears to be a puncturing of the anode glass layers. The cause of the puncturing is still somewhat obscure but the latter would seem to occur when rapidly moving ions like silver or sodium reach the anode layers.
3. The dielectric strength of the anode layers is not an intrinsic property of these layers but is also dependent upon the nature of the ions which reach them.

*Toronto, Canada,
October, 1927.*

CATALYTIC ACTIVITY OF TITANIA IN THE REDUCTION OF NITROCOMPOUNDS

BY G. ETZEL

Introduction

The first systematic investigation of the problem of hydrogenation was made by Sabatier¹ and his co-workers, principally Senderens and Mailhe at the close of the nineteenth century. Earlier investigators² however, had already shown the catalytic action of finely divided metals.

The work done by Sabatier and his assistants practically opened the field of research in hydrogenation, showing its application to the industry. The catalysts used were nickel, cobalt, iron, copper, platinum, and palladium. He found that by using nickel and cobalt in the hydrogenation of nitrobenzene by hydrogen, aniline, cyclohexylamine, ammonia, benzene, cyclohexane, dicyclohexylamine, cyclohexylaniline, and diphenylamine were obtained. Sabatier made an extensive study of catalytic reduction of several types of organic compounds.

A very complete and quantitative study on the reduction of nitrobenzene has been carried on since 1920 by O. W. Brown and his co-workers, principally C. O. Henke. The following catalysts were used: nickel, copper, silver, cobalt, iron, antimony, molybdenum oxide, manganese, chromium, vanadium oxide, uranium oxide, tungstic acid, cerium oxide, calcium oxide, barium oxide, tellurium, silica, alumina, lead, thallium, and bismuth. They showed that lead, bismuth, and thallium were the only catalysts to give high yields of azobenzene.

The only case known by the writer in which titania was used as a catalyst on reduction of nitrobenzene, is that of a few preliminary experiments made by O. W. Brown and Dr. F. A. Madenwald in this laboratory.

Purpose of Investigation

The purpose of this investigation was to make a thorough study of titania as a catalyst on the reduction of nitrobenzene. Conditions which were most favorable for the production of different compounds and their identification were sought. In order to obtain the maximum activity of the catalysts, efforts were made to find the most efficient temperature of ignition of the catalyst, temperature of reduction of the catalyst, rate of flow of hydrogen, rate of flow of nitrobenzene, and the temperature of reduction of nitrobenzene. The length of life of the catalyst, action of asbestos as a support, and the action of traces of manganese were also studied.

¹ Sabatier: "Catalysis in Organic Chemistry," 341-583 (1922).

² Kuhlmann: *Compt. rend.*, 7, 1107 (1838); Debus: *Ann.*, 128, 200 (1863); von Wilde: *Ber.*, 7, 352 (1874).

Apparatus and Method of Procedure

The apparatus as well as the method of procedure were the same as that followed by Brown and Henke.¹ The advantages of this apparatus are that it gives an accurate method of determining the temperature of the gaseous mixture while in contact with the catalyst, an easily regulated and accurately known rate of flow of nitrobenzene, and a means of quantitatively receiving the products.

The rate at which the hydrogen was passed into the furnace was measured by means of a flowmeter. A copper-constantan thermocouple was used to measure the temperature, and the voltage was read by a high resistance millivoltmeter.

Material used

In order to purify the material used, it was shaken with sodium carbonate solution and then distilled with steam. The distillate was dried with calcium chloride and redistilled twice. The hydrogen used was commercial hydrogen. It was purified by passing over red-hot scrap copper, caustic soda, through concentrated sulfuric acid, and then through a U-tube containing glass wool.

Estimation of Reduced Products

The product in the condenser was washed into a one liter flask, containing 25 cc. of concentrated hydrochloric acid, and then diluted to the mark. A portion of it was analysed for aniline in the same manner employed by Henke and Brown.² When azobenzene or hydrazobenzene was produced, it was filtered, dried and weighed. The method used by Sabatier and Senderens³ was followed to identify the cyclo compounds.

Preparation of the Catalyst

The catalyst was prepared by reducing titanium hydroxide in hydrogen. The titanium hydroxide was prepared by diluting 150 cc. of a 15% solution of titanium trichloride to one liter. After the solution had reached the boil, an excess of ammonium hydroxide was added. The precipitated titanium hydroxide was then filtered, washed free from chloride, and dried at 100°C. In most cases 14 g. of the catalyst was used. It was reduced at 302°C unless otherwise stated. The reduction was performed by passing hydrogen at the rate of 14 liters per hour during a period of one hour.

Effect of the Amount of Catalyst used

In order to determine the effects of different amounts of catalyst on the production of aniline, two furnaces were charged. One contained 6.8 g. of titanium hydroxide, and the other 14 g. The rate of flow of hydrogen, temperature of reduction, and all the other conditions were kept the same throughout a large number of experiments. It required about 16 experiments to obtain constant results, after which all the results were tabulated, as shown in Table I. The yields given are averages of from 2 to 4 experiments.

¹ Brown and Henke: *J. Phys. Chem.*, 26, 161-190 (1922).

² Henke and Brown: *J. Phys. Chem.*, 26, 161-190 (1922).

³ Sabatier and Senderens: *Ann. Chim. Phys.*, (8), 4, 319 (1905).

TABLE I

Temperature of reduction of catalyst—302°C.
 Rate of flow of hydrogen—14 liters per hour.
 Hydrogen passed in per cent of theory—573.
 Rate of flow of nitrobenzene—4.05 g. per hour.

Yields in % of amines calculated as aniline

| Temp. °C | Catalyst 14 g. | Catalyst 6.8 g. | Temp. °C | Catalyst 14 g. | Catalyst 6.8 g. |
|-------------|-------------------|--------------------|-------------|-------------------|--------------------|
| 264 | 50.1 | — | 310 | 84.31 | 89.93 |
| 275 | 82.85 | 42.8 | 320 | 75.98 | — |
| 282 | 85.43 | 62.08 | 358 | 60.1 | 75.91 |
| 291 | 88.86 | 63.74 | 395 | 28.9 | 58.15 |
| 302 | 89.83 | 88.1 | 431 | 11.8 | 31.34 |

It is evident from the results obtained that a broader curve is secured by using larger amounts of catalyst. In this manner higher yields are the result, at a wider range of temperature. At a temperature ranging from 273 to 302° C high yields are obtained with 14 g. of catalyst, while with 6.8 g. of catalysts, the high yields lay between 302 and 310°C showing a sudden drop when these limits are passed.

Effect of Rate of Flow of Hydrogen on the Production of Aniline

In studying the effect of the rate of flow of hydrogen, the best temperature for the production of aniline was selected, and the rate of flow of nitrobenzene, as well as all the other conditions, were kept constant. The results are given in Table II. The percents are averages of two experiments.

TABLE II

Weight of catalyst—14 g.
 Temperature of reduction of catalyst—302°C.
 Rate of flow of nitrobenzene—4.05 g. per hour.
 Temperature of reduction of nitrobenzene—302 C.
 Flow of hydrogen liters per hour = A.
 Hydrogen passed in % of theory = B.
 Yields in % of amines calculated as aniline = C.

| A | B | C | A | B | C |
|------|------|-------|----|-----|-------|
| 14 | 537 | 89.49 | 7 | 286 | 83.90 |
| 18 | 737 | 88.30 | 5 | 204 | 77.84 |
| 22 | 901 | 86.70 | 4 | 163 | 48.75 |
| 43.3 | 1778 | 80.56 | 14 | 537 | 77.90 |
| 30 | 1229 | 82.97 | | | |

It is evident from the results shown here that the best yields of aniline are obtained with the rate of flow of hydrogen at 14 liters per hour.

**The Effect of Rate of Flow of Nitrobenzene on the
Production of Aniline**

The catalyst used to determine the best rate of flow of nitrobenzene was reduced at 302°C. The temperature was kept constant, while the rate of flow of hydrogen varies with the rate of flow of nitrobenzene, maintaining the same excess of hydrogen throughout the different experiments. Results are tabulated in Table III.

TABLE III

Weight of catalyst—14 g.
 Temperature of reduction of the catalyst—302°C.
 Temperature of reduction of nitrobenzene—302°C.
 Hydrogen passed in per cent of theory—573.
 Flow of hydrogen liters per hour = A.
 G. nitrobenzene per hour = G.
 Yields in % of amines calculated as aniline = C.

| A | G | C | A | G | C |
|-----|------|-------|-----|------|-------|
| 8.8 | 2.36 | 66.16 | 15. | 4.37 | 79.5 |
| 9.6 | 2.8 | 66.26 | 26. | 7.13 | 78.75 |
| 9.7 | 3.15 | 74.59 | 32. | 9.4 | 76.10 |
| 14. | 4.05 | 85.30 | 49. | 14.2 | 63.45 |

It is obvious from these results that the rate of flow of nitrobenzene which produced the best yield of aniline was from 2.08 g. to 4.05 g. per hour. The highest yield was secured with a rate of flow of 4.05 g. per hour.

**Effect of Temperature of Ignition of Titanium Hydroxide on the
Reduction of Nitrobenzene**

To determine the best temperature of ignition of the catalyst, three furnaces were charged, the first with titanium hydroxide dried at 100°C., the second ignited at 245°C, and the third at 412°C.. All the conditions influencing the experiments were kept constant. The results became constant only after the sixteenth experiment, and those following this experiment are tabulated in Table IV. They are averages of from 2 to 4 experiments.

The results show that higher yields of aniline are obtained with the catalyst which was not previously ignited. In comparing the yields of aniline at any definite temperature a decrease is shown as the temperature of ignition increases. The only exception to this general rule was the temperature of 302°C, which gave a higher yield with the catalyst ignited at 245°C. The best yield was 93.5% aniline secured at 282°C with the non-ignited catalyst. The catalyst ignited at 415°C gave, at temperatures of 245 and 266°C, traces of azobenzene and hydrazobenzene. At higher temperature such as 340 to 430°C considerable amounts of ammonia and cyclo-compounds were produced. The production of ammonia and cyclo-compounds, as well as azobenzene and hydrazobenzene, was noticeably less with the catalyst ignited at 245°C. With the non-ignited catalyst no azobenzene and hydrazobenzene were produced. The production of ammonia and cyclo-compounds was also less with the non-ignited catalyst.

TABLE IV

Weight of the catalyst—14 g.

Temperature of reduction of the catalyst—302°C.

Rate of flow of nitrobenzene—4.05 g. per hour.

Rate of flow of hydrogen—14 liters per hour.

Hydrogen passed in per cent of theory—573.

| Temperature in degrees centigrade | Yields in % of amines calculated as aniline | | |
|-----------------------------------------|---------------------------------------------|---------------------------------|---------------------------------|
| | Catalyst not ignited | Catalyst ignited at 245°C | Catalyst ignited at 415°C |
| 226 | 75.86 | — | 60.4 |
| 245 | 84.54 | 71.04 | 79.50 |
| 264 | 91.40 | 80.41 | 78.03 |
| 282 | 93.50 | 82.87 | 82.21 |
| 302 | 85.35 | 86.80 | 52.94 |
| 340 | 60.45 | 66.55 | 38.38 |
| 360 | — | 19.18 | 14.88 |
| 395 | 16.80 | 8.60 | 3.30 |
| 430 | 6.61 | 6.51 | 1.32 |

Effect of Temperature of Reduction on the Production of Amines

The effect of temperature of reduction of the catalyst was studied. Four catalysts were reduced; the first at 260, the second at 203, the third at 360, and the fourth at 412°C. The rate of flow of hydrogen was 14 liters per hour, allowing an excess of 634% of hydrogen. The rate of flow of nitrobenzene was 4.05 g. per hour. The results obtained showed: (a) The best yield of aniline was 93.73% at a temperature of 282°C, with the catalyst reduced at 302°C. (b) The maximum yield with every catalyst was secured at 282°C. (c) Catalysts reduced at 360 and 412°C produced from 2 to 4% of azobenzene and hydrazobenzene at 206°C, and traces of them at 282°C, while with catalysts reduced at 360 and 302°C no azobenzene or hydrazobenzene were produced. (d) With catalysts reduced at 260°C the amount of aniline produced at 320°C was 39.09% as compared to 64.86% and 72.08% which were the yields obtained by the catalysts reduced at 360 and 412°C respectively, although the amount of ammonia and cyclo-compounds was considerably higher in the case of the catalyst reduced at 260°C than with the ones reduced at higher temperatures. (e) The aniline obtained with the catalyst reduced at 260°C had a yellowish color, while with the other catalyst it was cherry red.

It is obvious from these results that the best temperature of reduction of the catalyst for the production of aniline is 302°C, while for the production of cyclo-compounds it is 260°C.

Durability of the Catalyst and the Effect of Continuous and Intermittent Feeding of Nitrobenzene

A study was undertaken to determine the length of life of the catalyst. For this purpose experiments were carried on for several weeks, discontinuing only at night. In the first 58 experiments nitrobenzene was fed intermittently, leaving only 25 minutes after each 2 cc. to allow the hydrogen to wash any product from the furnace. After the 58th experiment from 8 to 10 cc. nitrobenzene was fed continuously each day for 11 days. Intermittent feeding was then resorted to again. The results secured are given in the following table.

TABLE V

Weight of the catalyst—14 g.

Temperature of reduction of the catalyst—302°C.

Temperature of reduction of nitrobenzene—302°C.

Hydrogen passed in per cent of theory—573.

Temperature in degrees centigrade = A.

Rate of flow nitrobenzene g. per hour = G.

Yields of amines in % calculated as aniline = C.

Number of cc. nitrobenzene fed = D.

| Nitrobenzene fed intermittently | | | | Nitrobenzene fed intermittently | | | |
|-----------------------------------------------|------|-------|----|-----------------------------------------------|------|-------|----|
| A | G | C | D | A | G | C | D |
| 282 | 4.05 | 51.31 | 8 | 302 | 4.37 | 80.74 | 2 |
| 302 | " | 31.37 | 2 | 302 | 2.8 | 74.59 | 2 |
| 320 | " | 25.41 | 4 | 302 | 2.36 | 66.1 | 2 |
| 360 | " | 11.11 | 4 | 302 | 9.5 | 80.08 | 2 |
| 395 | " | 3.75 | 2 | 302 | 4.05 | 89.38 | 2 |
| 432 | " | 2.42 | 2 | 282 | " | 93.74 | 4 |
| 282 | " | 80.50 | 2 | 264 | " | 91.42 | 4 |
| 302 | " | 85.62 | 36 | 302 | " | 84.35 | 4 |
| 302 | 4.37 | 79.50 | 2 | 320 | " | 60.45 | 2 |
| 302 | 7.13 | 78.75 | 2 | 395 | " | 16.80 | 2 |
| 302 | 4.05 | 86.69 | 2 | 432 | " | 6.11 | 2 |
| 302 | 14.2 | 63.45 | 2 | 245 | " | 87.02 | 4 |
| 302 | 9.4 | 76.10 | 2 | 228 | " | 75.89 | 4 |
| 302 | 2.36 | 66.16 | 4 | 245 | " | 82.05 | 4 |
| Nitrobenzene fed continuously during each day | | | | Nitrobenzene fed continuously during each day | | | |
| 282 | 4.05 | 90.43 | 8 | 282 | 4.05 | 88.02 | 4 |
| 282 | " | 93.07 | 8 | 282 | " | 85.55 | 14 |
| 282 | " | 85.55 | 10 | 282 | " | 85.42 | 8 |
| 282 | " | 93.07 | 8 | 282 | " | 93.07 | 2 |
| 282 | " | 91.40 | 8 | 282 | " | 90.43 | 8 |
| 282 | " | 90.43 | 8 | 282 | " | 88.02 | 6 |
| 282 | " | 94.64 | 8 | | | | |
| Nitrobenzene fed intermittently | | | | | | | |
| 282 | 4.05 | 90.69 | 8 | | | | |

Results showed that at the end of 112 experiments, which were performed during a period of several weeks, the catalyst was still giving its maximum yield of aniline. There was practically no difference in the results obtained when nitrobenzene was fed continuously or intermittently. However, slightly higher results were secured when it was fed continuously. With every catalyst used, the first 16 experiments gave percent yields that were low and somewhat irregular. But it was found that by feeding nitrobenzene at the temperature of 430°C or by passing hydrogen at the same temperature for one hour, the activity of the catalyst was increased for the production of aniline and was decreased for the production of ammonia and cyclo-compounds.

The color of the aniline produced was in most experiments cherry red. But after passing nitrobenzene at 430°C the color changed for a few experiments to a light yellow, later returning to a cherry red when a low temperature was used. This seems to indicate that the color is probably due to small traces of azobenzene in solution. By heating the catalyst to a high temperature the azobenzene in the furnace was entirely washed out. As the azobenzene was reformed slowly, the aniline turned red again.

Identification of Cyclo-compounds

In all the experiments performed it was noted that not only ammonia but also cyclo-compounds were being produced. In order to identify cyclo-compounds a large vertical furnace containing 30 g. of reduced catalyst was set up. About 70 cc. of nitrobenzene was introduced into the furnace. The temperature was 430°C while the other conditions were the same as those in previous experiments. The product obtained was dried over calcium chloride and submitted to fractional distillation. Three fractions were obtained: one boiling below 150°C, another boiling from 150 to 180°C, and the other was the residue left in the distilling flask. The first two fractions were mixed and submitted again to fractional distillation. At a temperature of about 100°C, white crystals were deposited in the condenser tube. They were recrystallized and appeared to correspond to cyclohexylamine carbonate.

The fraction which remained in the distilling flask was fractionally distilled under a 5 in. reduced pressure to avoid any decomposition of the compounds. Two fractions were secured; one boiling at 190°C, and the other was a residue which was solid. The residue corresponded to diphenylamine. The portion which was distilled under 109°C was redistilled at atmospheric pressure. Most of the solution boiled at 182°C, which is the boiling point of aniline.

It is evident from this that cyclo-compounds are obtained, cyclohexylamine and diphenylamine being formed in large amounts.

Effect of Asbestos as a Support on the Titania Catalyst

The effect of asbestos as a support for titania was determined. The catalyst was prepared in the following manner. Clean asbestos was boiled with concentrated hydrochloric acid, washed free from chloride, and dried in an electric muffle. It was then soaked in a boiling solution of 100 cc. of 15% titanium

trichloride diluted to 500 cc., treated with ammonium hydroxide, filtered, and dried at 100°C. Since the weight of asbestos was known, from the total weight the percent of titanium hydroxide was calculated. The catalyst used contained 5 g. of asbestos and 7 g. of titanium hydroxide. It was reduced at 302°C and the rate of flow of hydrogen used was 14 liters per hour, while the rate of flow of nitrobenzene was 4.05 g. per hour. The results obtained showed that there is no advantage in using asbestos as a support for the catalyst. The yields obtained were practically the same as those of the catalyst consisting of the same weight of titanium alone. Also the color of aniline was not improved. The average yields secured were: 79.79% at 282°C, and 76.6% at 320°C. Although asbestos did not improve the yields, its presence did not reduce the activity.

Effect of Traces of Manganese on Titania

The catalyst used to determine the effect of traces of manganese on titania was prepared by dissolving a calculated amount of manganese chloride in water mixed with 100 cc. of a 15% solution of titanium trichloride diluted to one liter and precipitated with ammonium hydroxide. The manganese and titanium precipitates were filtered and washed free from chloride, then dried at room temperature. Fourteen grams of the catalyst was used. It contained 5% of manganese and 95% of titania, and was reduced at 302°C. The rate of flow of hydrogen used was 14 liters per hour, and the rate of flow of nitrobenzene 4.05 g. per hour. The best yields obtained were 89.96% at 282°C., 82.32% at 246°C.

The yields of aniline did not improve but the presence of manganese prevented the formation of azobenzene. The color of aniline was improved. At first it was light yellow, then it turned to a very light red, after having been used for several experiments.

This problem was suggested by Prof. O. W. Brown. I wish to thank him for his suggestions and interest throughout this investigation.

Conclusion

1. Titania was shown to be a very active catalyst of the nickel and cobalt type. It produced, on the reduction of nitrobenzene, the following compounds: aniline, azobenzene, hydrazobenzene, ammonia, and cyclo-compounds.
2. The catalyst used in this study was made from titanium hydroxide which was prepared by precipitation with ammonium hydroxide from a 15% solution of titanium trichloride.
3. In making a comparison of the weight of the catalyst on the reduction of nitrobenzene, it was found that higher yields were obtained with 14 g. catalyst than with 6.8 g. This shows that the yield of amines increases with the amount of catalyst.
4. The best temperature for carrying out reduction of nitrobenzene to aniline was about 282°C.
5. The best yield of aniline was 94.4% or an average of 93.5% obtained at about 282°C with catalyst reduced at 302°C.

6. The most favorable temperature of ignition of titanium hydroxide for the reduction of nitrobenzene to aniline was 100°C . Those ignited at 302 and 412°C were the best for the production of azobenzene and hydrazobenzene.

7. The rate of flow of hydrogen which gave the highest yield of aniline was 14 liters per hour, with 14 g. of catalyst. A gradual drop occurred as the volume of hydrogen increased, and a more sudden drop when it decreased.

8. The rate of flow of nitrobenzene giving the best results with a 14 g. catalyst was found to be from 2.02 to 4.05 g. per hour, the best being 4.05 g. per hour.

9. Practically no difference was found in the yields of aniline when nitrobenzene was fed continuously or intermittently.

10. The activity of the catalyst was poor and gave results that were somewhat irregular up to the 16th experiment. After that it became constant.

11. After heating the reduced catalyst for one hour in hydrogen at a temperature of 410°C , or by passing nitrobenzene at that temperature for one or two experiments, its activity was increased for the production of aniline.

12. The temperature of reduction of the catalyst that was most successful was 302°C . Although the catalyst reduced at 260°C did not give maximum yields, they were high, and the color of aniline was improved.

13. The color of aniline produced was slightly yellow with the catalyst reduced at 260°C , while with those reduced at a higher temperature it was cherry red.

14. Identification of cyclo-compounds showed the presence of cyclohexylamine and diphenylamine.

15. Although asbestos did not produce higher yields of aniline, its presence did not reduce the activity of the catalyst.

16. Traces of manganese did not improve the yields of aniline, but gave a product of better color.

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STUDIES IN THE EXPERIMENTAL TECHNIQUE OF PHOTOCHEMISTRY

V. Reflection Losses in the Optical System of the Hilger Ultra-Violet Monochromatic Illuminator

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Introductory

In earlier papers in this series¹ an account was given of the use of the Hilger Monochromatic Illuminator for the determination of energy distribution in light sources. In the latter of these² the authors considered the question of reflection at the mirror and quartz surfaces of the spectrometer.

In the case of the mirror they gave figures for the reflections at different wave-lengths, determined by a method, which although the only one available without special apparatus, was of very doubtful accuracy.

In the case of reflections at the quartz surfaces, it was stated that, as the change in reflection with wave-length is small, it can be neglected. This might be true for one surface at normal incidence; but in this instrument are several surfaces, with, in some cases, large angles of incidence, and correspondingly greater changes of reflection coefficient with wave-length. Thus the small change is repeated several times, with the result that it becomes very appreciable in total.

Greater accuracy being now more important, this matter has been carefully investigated. Special apparatus has been constructed to measure the reflection of the mirror at various wave-lengths, while the reflections at the quartz surfaces have been calculated, using the formulae

$$\left(\frac{n-1}{n+1}\right)^2 \quad (1)$$

for normal incidence, and

$$\frac{1}{2} \left[\frac{\sin^2(I-R)}{\sin^2(I+R)} + \frac{\tan^2(I-R)}{\tan^2(I+R)} \right] \quad (2)$$

where I is the angle of incidence, R is the angle of refraction, for other cases.

The total percentage of light passing the collimator slit of the instrument, which is transmitted to the thermopile, has been calculated for a number of wave-lengths; and also factors by which galvanometer deflections should be multiplied in order to compare them with $579 \mu\mu$, which is taken as standard for this purpose.

Apparatus

The mirror in the spectrometer consists of a quartz plate backed with a white metal—possibly tin amalgam. The angle of incidence to this metal in the instrument varies between $15^\circ 32'$ at $579 \mu\mu$ and $13^\circ 32'$ at $254 \mu\mu$. As

¹ J. Phys. Chem., 29, 39-57; 713-726 (1925).

² Pp. 722, 724.

such a small angle of incidence introduced numerous practical difficulties, the actual experimental work was carried out with the light incident at 45° to the quartz-air surface, the resulting angles to the metal being $27^\circ 14'$ at $579\mu\mu$ and $26^\circ 16'$ at $254\mu\mu$.

The apparatus employed is shown in Fig. 1. The spectrometer H. J. with its associated thermopile K and Paschen galvanometer, were used to measure the relative intensities of the direct and reflected beams. A triangular brass frame was supported at the base by two legs, adjustable in length, and carrying at their lower ends small wheels; and at the apex by a pivot placed vertically below the optical axis H - J of the collimator of the spectrometer. The frame could thus rotate over a smooth metal surface between the stops LL, through an angle of 90° . This frame carried a quartz mercury lamp B (the supports of which are not shown), and, on the pivot side of this, a copper screen, on which is fixed a small diaphragm D, adjustable in position. It also carried a lens E of 12.5 cms. focal length, mounted upon a slide to enable the lens to be focussed for parallel light at any wave-length. This slide consisted of a brass carrier sliding upon two silver-steel bars, these being supported by a plate, which was attached to the frame by a screw passing through a slot, thus allowing a lateral and rotary movement of the slide. Vertical adjustment of the lens was provided for in the carrier. A focussing scale was attached to the frame.

Immediately above the pivot was placed the mirror mounting A. This is shown in greater detail in the small diagram (Fig. 1). The mirror M was clamped on the foremost of two brass plates NN by four small clips OO. These plates were held together by two screws PP, and kept apart by two others Q. These screws enabled the angle of the mirror to be adjusted. The rear plate was supported above the level of the frame by two bars RR, through the lower end of which passed a silver steel spindle S, running in bearings fixed upon a plate attached to the frame. This arrangement permitted the mirror to be swung up and down without any side-play. When in a vertical position the back of the plates supporting the mirror rested against a screw V, which passed through a stout vertical pillar W, and could be secured by the lock nut X. The top of W was, of course, below the level of the mirror itself. Two strings attached to these plates and to the bench, one of them passing through a hole in W, caused the plates to be drawn firmly back against the screw V as the frame swung into the 'reflected' position, and to be lowered when it was moved into the 'direct' position.

After leaving the mirror the light was concentrated upon the slit H by another lens G, which was fixed in position.

This form of apparatus was evolved after considerable experimental work. The two surfaces of the mirror cause a number of images, three of which are important. In earlier work attempts were made to separate these and measure the principal one, due to one reflection from the metal, with corrections

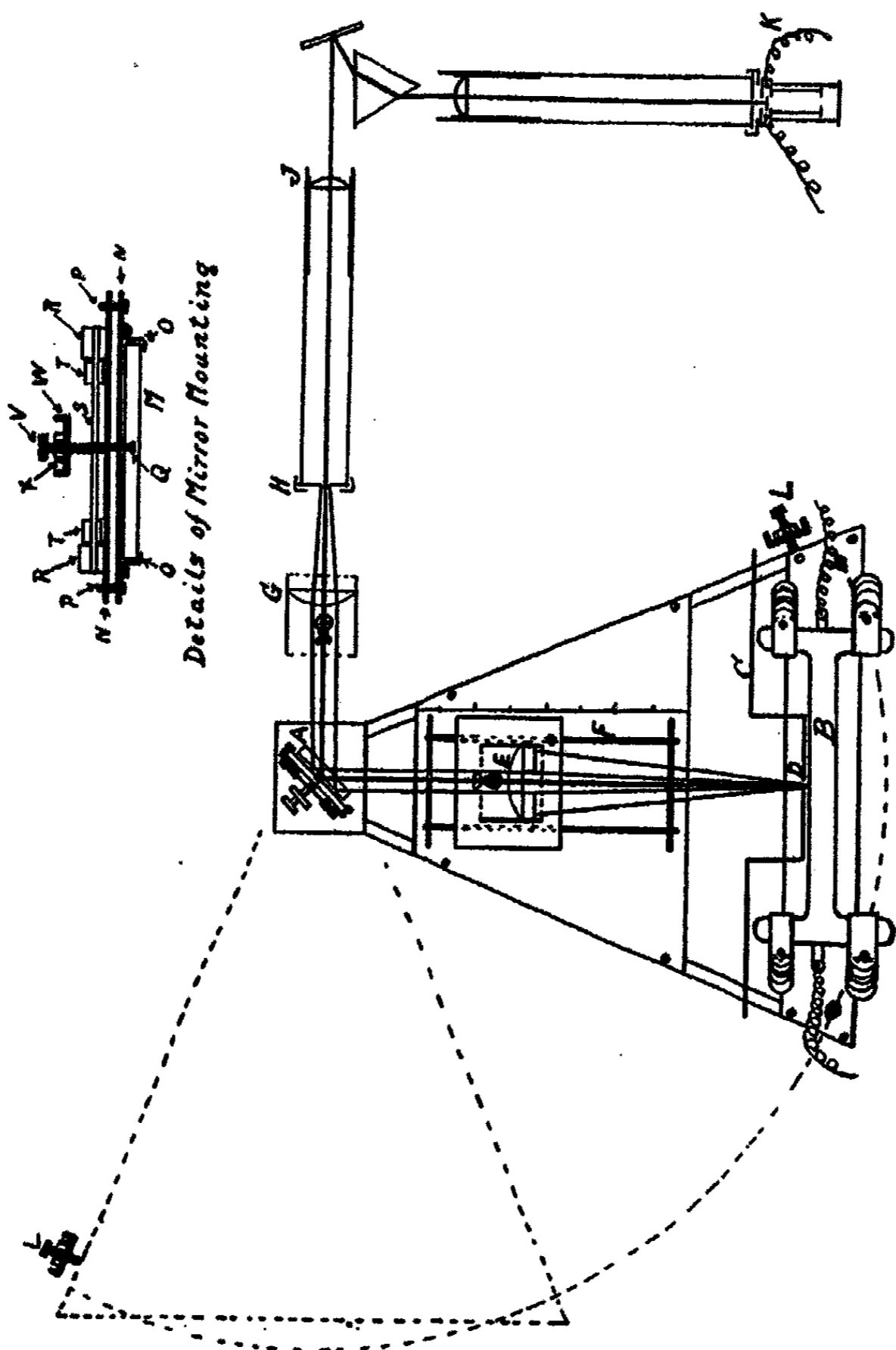


Fig. 1
Apparatus for determining Reflection Coefficients.

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for back reflections from the quartz. Results obtained thus afforded rough confirmation of the final results. In the apparatus as described, experiment showed that these images were not appreciably separated at the collimator slit. It was found to be very important to have the light incident upon the mirror as exactly parallel as possible.

Adjustment

During preliminary measurements, some considerable difficulty was encountered in making the necessary adjustments. The method finally adopted is given below.

The height of the two legs of the frame were adjusted until the frame was level. The height of the mercury lamp B was then fixed, so that the centre of the arc tube was approximately on the optical axis of the collimator H — J when in the 'direct' position. A ground glass screen, suitably divided horizontally and vertically, was placed behind the collimator lens J, where it received an image of the slit H. The diaphragm D was then adjusted until this image was exactly central upon the screen. The lens E was next adjusted, and simultaneously the position of the slide F, so that in whatever position the lens was placed upon the slide, the image was still central upon the screen, while at the same time the image of D upon the collimator slit was symmetrically placed; showing that the slide was parallel to the optical axis, and the lens at the right height, etc.

The frame was then moved into the 'reflected' position, and the mirror adjusted. This was done by means of the screw V, controlling the position of the mirror relative to the axis of rotation of the frame, and the screws PP, Q, controlling the angle at which it is inclined to the optical axis of the apparatus.

When the images on the slit and the ground glass screen were again central, as described above, the mirror was considered correctly placed.

Finally the lens G was fixed, using the same criteria.

Method

Measurements of the relative intensities of the two beams were made by taking galvanometer deflections in pairs, alternately in the 'direct' and 'reflected' positions, until a satisfactory series of figures had been obtained. The lamp was unaffected by the movement.

In order to test the absolute accuracy obtainable, measurements were made of the reflecting power of a single quartz-air surface, obtained by grinding one side of an optically flat quartz plate, and coating the ground surface with a suspension of lamp black in Canada balsam; the polished surface being used for the reflection. The results obtained are compared below with the calculated figures.

| Wave-Length | Reflected Ray (observed) | Reflected Ray (Calc. from Formula 2) |
|-------------|-----------------------------|-----------------------------------------|
| 579 | 5.51% | 5.66% |
| 546 | 5.24% | 5.68% |
| 436 | 5.72% | 5.78% |
| 405 | 5.87% | 5.84% |
| 365 | 5.78% | 5.92% |
| 313 | 6.1 % | 6.08% |
| 265 | 6.2 % | 6.33% |

Results

Two mirrors were examined, the one not mounted on the frame being used in the spectrometer. The results are given in Table I.

TABLE I

| Wave-Length | Mirror A | | Mirror B | Working Mean |
|-------------|----------|-------|----------|--------------|
| 579 | 67.2% | 67.5% | 66.1% | 67% |
| 546 | 67.2 | | 66.0 | 67 |
| 436 | 65.7 | 67.1 | 68.9 | 67 |
| 405 | 66.4 | 66.1 | 66.2 | 66.5 |
| 365 | 67.0 | | 67.7 | 67 |
| 313 | 65.2 | 65.3 | 69.0 | 66 |
| 265 | 64.9 | | 64.8 | 65 |
| 254 | 62.1 | | 64.0 | 63 |

There is thus a small difference between the two mirrors, but as these were supplied at times several years apart, it seems that the 'working mean' given is likely to give results accurate to 1% in most cases.

The reflection losses at the quartz surfaces in the spectrograph were then calculated, using the formulae above, and treating the lens surfaces as plane. The optical system is shown on Fig. 2. It will be seen from this that every angle in the system is defined by the deviation, and the prism is in the position of minimum deviation. A list of refractive indices, taken chiefly from Rubens' figures,¹ together with the semi-deviations calculated from these, was given in Messrs. Hilgers' notes on the instrument. From these figures the various angles of incidence and refraction, and the corresponding percentage reflections, were obtained. The values for the mercury lines were found by interpolation, and those in the Ultra-Violet are given with the calculated figures in Table II.

¹ Rubens: Ann. Physik, (3) 60, 434 (1897).

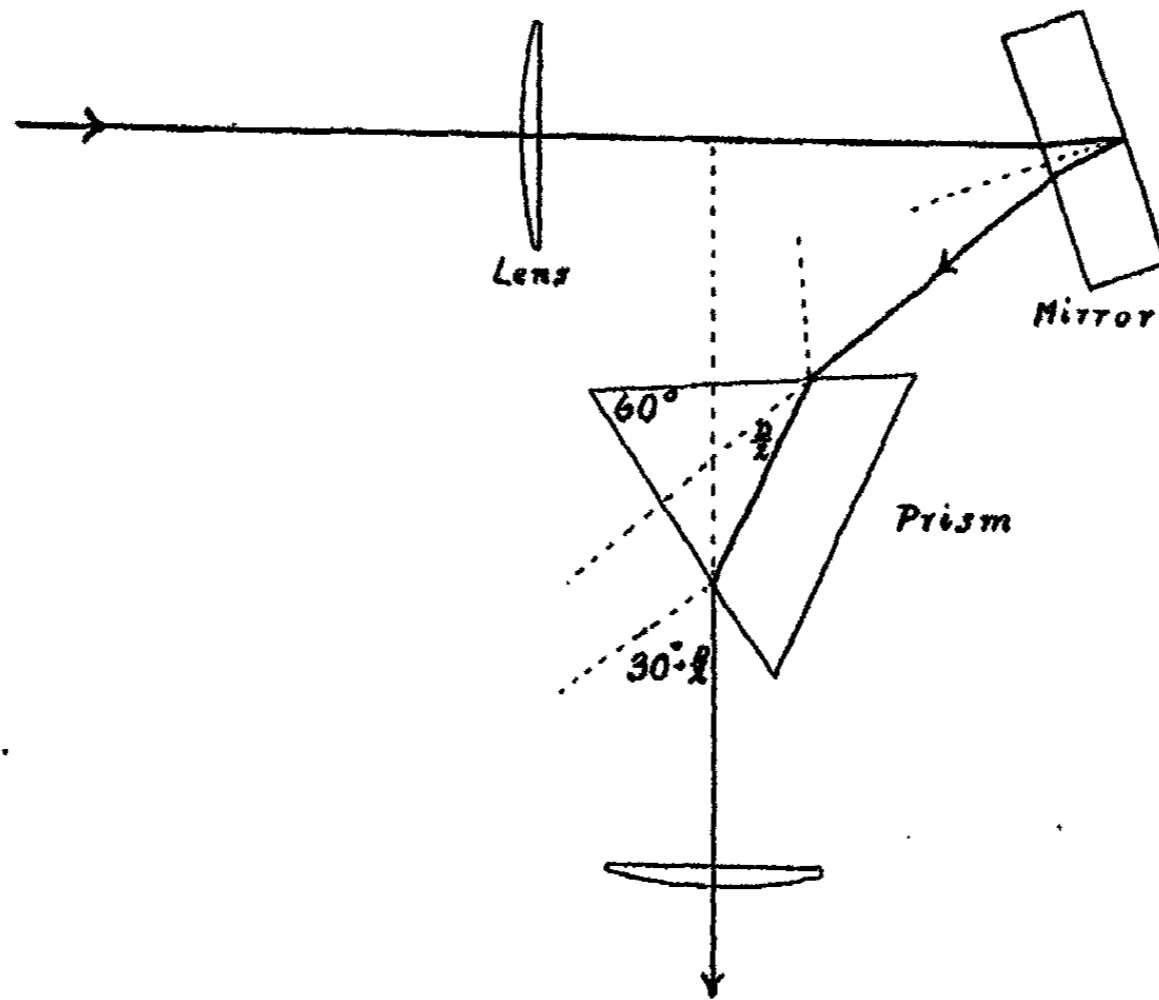


FIG. 2

Diagram showing Passage of Light through Hilger Spectograph.

TABLE II
Reflections at Quartz Surfaces

| Wave- Length ($\mu\mu$) | Refractive Index (n). | Semi- Deviation (D/2). | Reflections (%) | | | |
|---------------------------------|-----------------------------|------------------------------|----------------------|---------|-------------------|------------------|
| | | | Normal Incidence. | I = 45° | I = 30° - D/2. | I = 45° - D/2 |
| 198.81 | 1.65070 | 25° 17' 26'' | 6.03 | 7.18 | 9.04 | 6.05 |
| 231.25 | 1.61402 | 23° 48' 17'' | 5.52 | 6.64 | 8.17 | 5.56 |
| 248 | 1.6008 | | 5.35 | 6.45 | 7.91 | 5.41 |
| 254 | 1.5972 | | 5.28 | 6.39 | 7.84 | 5.36 |
| 265 | 1.5917 | | 5.21 | 6.31 | 7.71 | 5.28 |
| 247.67 | 1.58750 | 22° 32' 15'' | 5.15 | 6.26 | 7.62 | 5.20 |
| 280 | 1.5852 | | 5.12 | 6.23 | 7.55 | 5.19 |
| 303 | 1.5772 | | 5.01 | 6.11 | 7.35 | 5.08 |
| 313 | 1.5741 | | 4.98 | 6.08 | 7.27 | 5.03 |
| 317.98 | 1.57290 | 21° 51' 18'' | 4.96 | 6.06 | 7.24 | 5.01 |
| 358.18 | 1.56400 | 26' 39'' | 4.84 | 5.93 | 7.01 | 4.88 |
| 365 | 1.5629 | | 4.82 | 5.91 | 6.98 | 4.88 |
| 404.58 | 1.55706 | 7' 34'' | 4.75 | 5.83 | 6.84 | 4.81 |
| 434.09 | 1.55387 | 20° 58' 51'' | 4.70 | 5.78 | 6.76 | 4.77 |
| 486.16 | 1.54961 | 47' 14'' | 4.65 | 5.72 | 6.65 | 4.71 |
| 534.96 | 1.54663 | 39' 10'' | 4.61 | 5.68 | 6.58 | 4.67 |
| 589.32 | 1.54415 | 32' 26'' | 4.57 | 5.65 | 6.52 | 4.64 |
| 656.33 | 1.54181 | 26' 6'' | 4.54 | 5.61 | 6.46 | 4.61 |

It was stated earlier that the experimental work was carried out at a different angle from that used in the spectrograph. There are no data available to enable a correction to be applied in the case of the metal, but it was pointed out that the difference in angle of incidence at the metal surface was less than the difference in the case of the quartz-air surface. The reflection coefficient was corrected for this latter, but was found to be only -0.1% in each case. The true reflection of the metallic surface was found to be 0.6% less than the percentages given for the mirror, except for $254\mu\mu$, which was 62.2% , and $265\mu\mu$, 64.3% .

From the various results in these tables, the total percentage of light transmitted by the spectrometer was calculated, taking the system as having 4 plane surfaces, 2 prism surfaces, and the mirror. From these figures, the factors by which it is necessary to multiply galvanometer deflections in order to reduce all lines to the basis of $579\mu\mu$, were obtained. These percentages and factors are given in Table III.

TABLE III

| Wave-Length | Transmission | Factor |
|-------------|--------------|--------|
| $254\mu\mu$ | 43.1% | 1.13 |
| 265 | 44.6 | 1.09 |
| 313 | 46.2 | 1.05 |
| 365 | 47.5 | 1.02 |
| 405 | 47.5 | 1.02 |
| 436 | 48.0 | 1.01 |
| 546 | 48.4 | 1.00 |
| 579 | 48.5 | 1.00 |

Summary

The reflection of the Mercury Lines by the mirror in the Hilger U. V. Monochromatic Illuminator has been studied experimentally.

The reflection losses at the various quartz surfaces in this instrument have been calculated.

From these figures the total transmissions of the mercury lines have been calculated, together with factors to reduce results obtained with the instrument to a common basis.

The writers wish to express their deep gratitude to Professor A. J. Allmand for continual help and encouragement in the course of this work. They also wish to thank Mr. W. E. Williams, of the Physics Staff of this College, for most helpful advice; and Messrs. Adam Hilger for the loan of one of the two mirrors used in this work. One of us (D.W.G.S.) is indebted to the Department of Scientific and Industrial Research, for a grant while a Student in Training.

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January 18, 1928.*

2508.244

A CONTRIBUTION TO OUR KNOWLEDGE OF DISINFECTANT ACTION. II

The Relations of Phenols and Amines to Proteins

BY E. ASHLEY COOPER AND JOHN MASON

In the previous paper¹ it was shown that phenol and resorcinol were distributed between water and proteins in accordance with the partition-law, i.e. the phenols formed a true solution in the protein phase. This relationship is of an unusual type in the case of colloids, owing to surface phenomena such as adsorption, the amount of substance taken up or adsorbed by the colloid diminishing relatively with rise in concentration.

It was also found that resorcinol was somewhat more soluble in dispersed or dissolved proteins than phenol, although the latter is considerably more potent as a disinfectant. The conclusion was therefore drawn that, although partition of the disinfectant between water-phase and cell proteins is an essential preliminary stage in disinfection, yet germicidal power is not merely determined by solubility, but must be associated with the subsequent denaturing action on the colloidal structure of the bacterial cell.

In order to throw more light on the rôle of the preliminary process of *solution* in the mechanism of disinfection the work has been extended to other phenolic derivatives, e.g. picric acid and salicyl-sulphonic acid, and furthermore the relationships to proteins of disinfectants of a different type altogether, such as amines, has also been studied.

I. Picric Acid

Walker and Appleyard² showed that when picric acid was taken up by silk from aqueous solution, the partition law did not apply, and the process was clearly one of adsorption.

It seemed desirable to extend this work to other proteins, and for this purpose serum albumin was employed. 1 grm. of powdered coagulated albumin was immersed in 30 cc. of each of a series of aqueous picric acid solutions, concentrations varying from 0.2% to 1.5%. The experiment was conducted at 37°C. The period required for the completion of adsorption was determined by preliminary experiment. The estimation of picric acid before and after adsorption was carried out by titration of the solutions with N/20 alkali, lacmoid being used as indicator.

The results in Table I show that the amount of picric acid taken up by the protein increases with rise in concentration in the water, but not proportionately, so that the ratio of the concentration of picric acid in the protein to that in the water phase diminishes with increasing concentration. The results are similar to those obtained by Walker and Appleyard (*loc. cit.*) with

¹ Cooper and Sanders: *J. Phys. Chem.*, 31, 1 (1927).

² Walker and Appleyard: *J. Chem. Soc.*, 69, 1349 (1896).

silk. The uptake of picric acid by proteins is thus of the nature of adsorption or surface concentration, in contradistinction to the formation of a solution in the colloid phase. (cf phenol.) Phenol was previously found to be about 12 times as soluble in serum-albumin as in water, whereas the foregoing results show that the amount of picric acid adsorbed by the protein is from 27 to 922 times as great as the amount remaining in the aqueous solution at equilibrium. Picric acid is a much more efficacious disinfectant and protein-precipitant than phenol, and we have therefore in this case some measure of correspondence between germicidal activity and uptake by proteins.

TABLE I.

| | Uptake of picric acid by 1 gm. albumin. A | Initial conc. of picric acid per cc. of water phase | Final conc. of picric acid per cc. of water phase. B | Ratio A/B |
|-----|-------------------------------------------------------|-----------------------------------------------------------------|------------------------------------------------------------------|--------------|
| (1) | .2441 gm. | .01583 gm. | .00771 gm. | 31.6 |
| | .1785 | .01246 | .00652 | 27.4 |
| | .1840 | .00992 | .00383 | 48.0 |
| | .1454 | .00521 | .00039 | 374.0 |
| | .0587 | .00211 | .00017 | 345.0 |
| (2) | .2788 | .01475 | .00547 | 51.0 |
| | .2780 | .01214 | .00288 | 96.6 |
| | .2678 | .01196 | .00304 | 88.2 |
| | .2704 | .01214 | .00313 | 86.3 |
| | .2412 | .00894 | .00090 | 268.7 |
| | .2081 | .00744 | .00051 | 407.9 |
| | .1756 | .00624 | .00039 | 451.9 |
| | .1447 | .00510 | .00028 | 517.8 |
| | .1345 | .00461 | .00015 | 922.5 |
| | .0612 | .00218 | .00015 | 420.0 |

II. Salicylsulphonic Acid

This substance is employed in medicine as a protein-precipitant, and has also been found to be moderately active as a germicide, being efficacious in concentrations of 1 in 300. A study of the nature of the distribution of salicylsulphonic acid between proteins and water was therefore undertaken.

(a). Gelatin.

Weighed amounts (1 gm.) of gelatin in the form of small strips ($\frac{1}{2}$ by $\frac{1}{2}$ ins.) were immersed in aqueous solutions of salicylsulphonic acid (30 cc.) at 20°C until equilibrium was attained (5 days). The strength of the initial and final solutions was determined by titration with N/10 alkali, using phenolphthalein as indicator. The results are set out in Table II.

| Initial conc. of acid per cc. in water phase | Amount of acid taken up by 1 gm. gelatin. | | Final conc. of acid per cc. in water phase. | Ratio A/B | Physical state of protein |
|----------------------------------------------|-------------------------------------------|------------|---------------------------------------------|------------|---------------------------|
| | A | B | | | |
| .00216 gm. | .0328 gm. | .00106 gm. | 30.8 | Swollen | |
| .00517 | .0474 | .00360 | 13.2 | " | |
| .00805 | .0453 | .00654 | 6.9 | " | |
| .01998 | .0993 | .01669 | 5.9 | " | |
| .03488 | .1502 | .02989 | 5.0 | Opalescent | |
| .04889 | .1545 | .04376 | 3.5 | Solid | |

(b). *Albumin.*

This protein is soluble in water, and it was therefore necessary to use a different technique, viz. the dialysis method. Into a number of bottles (wide-mouthed), viscous dialysers were placed, and within each dialyser were introduced 20 cc. of a 6% egg-albumin solution. Outside the dialysers 30 cc. of salicylsulphonic acid solutions, of different strengths, were placed. Control bottles were set up, containing 20 cc. of water within the dialyser and 30 cc. of the acid solutions outside. By titrating the solutions outside the dialysers after standing for equilibrium to be attained, the amount of salicylsulphonic acid taken up by the protein in equilibrium with the water phase could be ascertained. The results are given in Table III.

| Initial conc. of acid per cc. of water-phase | Amount of salicylsulphonic acid taken up by 1 gm. of protein | | Final conc. per cc. of water phase. | Ratio A/B |
|----------------------------------------------|--------------------------------------------------------------|------------|-------------------------------------|-----------|
| | A | B | | |
| .00309 gm. | .0704 gm. | .00133 gm. | 53.1 | |
| .00614 | .1344 | .00276 | 48.7 | |
| .01239 | .1972 | .00743 | 26.5 | |
| .02102 | .2266 | .01534 | 14.7 | |
| .02890 | .2266 | .02322 | 9.7 | |
| .05575 | .2113 | .05045 | 4.2 | |
| .08105 | .2207 | .07553 | 2.9 | |

The results are again similar in type to those obtained in the case of picric acid, the amount of salicylsulphonic acid taken up by the proteins diminishing *relatively* with rise in concentration in water-phase, thus causing a marked fall in the magnitude of the distribution ratio A/B from 53 to 3. It is also of interest to note that the distribution ratio is lowest when the protein is in the precipitated condition (Table II.). In the case of phenol, however, it had previously been found¹ that the partition-coefficient was much higher (12) for precipitated proteins than for proteins in colloidal solution (2.5).

¹ Cooper and Sanders: loc. cit.

III. Ethylamine

Although organic bases are known to be efficacious germicides, (ethylamine, for example, being antiseptic¹ in concentrations of 1 in 1500, and thus more powerful than phenol), their relations to proteins have not apparently been previously investigated. Weighed amounts of gelatin (1 gm.) as before were therefore immersed in 50 cc. of various concentrations of ethylamine in water (.3%-3%), and by titrating the initial and final concentrations with standard acid, the amount of amine taken up by the proteins could be estimated. The period allowed for equilibrium was 2 days. The results are given in Table IV.

TABLE IV

| Initial conc. of ethylamine per cc. of water phase | Amount of ethylamine taken up by 1 gm. of protein A | Final conc. of ethylamine per cc. of water phase B | Ratio A/B |
|----------------------------------------------------|--------------------------------------------------------|-------------------------------------------------------|--------------|
| .00329 gm. | .0198 gm. | .0029 gm. | 6.8 |
| .00650 | .0199 | .0061 | 3.2 |
| .01307 | .0234 | .0126 | 1.9 |
| .01981 | .0254 | .0193 | 1.3 |
| .02651 | .0307 | .0259 | 1.2 |

Again the adsorption factor predominates, the distribution ratio falling from 6.8 to 1.2 as the concentration in water-phase rises.

IV. Aniline

Aniline can be estimated in aqueous solution by titration with standard hydrochloric acid, using either bromphenol-blue or Congo Red as indicator. The former was found more sensitive and therefore employed.

1 gm. of gelatin was introduced into 50 cc. of solutions of aniline (.2%-2%), and the experiment carried out as before. The results are given in Table V.

TABLE V

| Initial conc. of aniline per cc. of water-phase | Uptake of aniline per gm. of protein A | Final conc. per cc. of water-phase B | Ratio A/B |
|-------------------------------------------------|-------------------------------------------|-----------------------------------------|--------------|
| .01890 gm. | .0549 gm. | 0.178 gm. | 3.0 |
| .01580 | .0397 | .0150 | 2.7 |
| .01205 | .0274 | .0115 | 2.4 |
| .00912 | .0411 | .0083 | 4.9 |
| .00630 | .0000 | .0063 | — |
| .00358 | .0034 | .0029 | 1.2 |
| .00212 | .0108 | .0019 | 5.7 |

¹ Cooper and Mason: J. Hygiene, 26, 48 (1927).

The analytical method was less precise in the case of aniline than the foregoing experimental work, and it was not surprising therefore to find irregularities in the value of the distribution ratio A/B. This ratio however tends to fall with rising concentration, suggesting again an adsorption process.

V. Hydrazine Hydrate

Hydrazine hydrate was found to be¹ a very powerful germicide, being active in concentrations of 1 in 20,000. Its behaviour towards proteins was therefore of interest. Distribution experiments, using gelatin, were carried out in the usual way, the hydrazine being estimated by an iodimetric method. It was found however, that hydrazine was not adsorbed by the protein; in fact, the solutions appeared to become slightly stronger, suggesting therefore a condition of "negative" adsorption. The solute was more concentrated in the aqueous phase than at the surface of the colloid.

VI. Hydroxylamine Hydrochloride

This substance was also found to be active against bacteria, being inhibitory in concentrations of 1 in 10,000. Hydroxylamine hydrochloride is also a protein precipitant in dilutions of 1 in 400 to 1 in 1500. Stronger solutions however have no precipitating action, the protein being soluble in excess.

The uptake of the hydrochloride by egg-albumin was therefore next studied. The estimation was carried out by the methods:—

(1) Titration of the hydrochloride with standard alkali, using phenolphthalein as indicator.

(2) Raschig's method, consisting in the oxidation of the hydroxylamine with ferric salts, and estimation of the equivalent amount of ferrous compound produced by titration with permanganate.

20 cc. of a solution of egg-albumin (.47 gm.) were placed in a series of viscose thimbles, surrounded in stoppered bottles by 30 cc. of solutions of hydroxylamine hydrochloride of known concentrations. Control solutions without albumin were set up at the same time. After allowing a week for equilibrium to be attained, the strength of the external solutions was again estimated by titration with alkali; and by difference the amount of hydroxylamine hydrochloride taken up by the protein could be ascertained. The results were tabulated in Table VI.

| Initial conc. of NH ₂ OH.HCl per cc. of water phase | Weight of NH ₂ OH.HCl taken up by 1 gm. albumin A | Final conc. of NH ₂ OH.HCl per cc. of water phase B | Ratio A/B |
|----------------------------------------------------------------------|-----------------------------------------------------------------------|-------------------------------------------------------------------------|--------------|
| .0297 gm. | .0000 gm. | .0297 gm. | 0.0 |
| .01196 | .0170 | .0118 | 1.4 |
| .00802 | .0239 | .0078 | 3.0 |
| .0060 | .0316 | .0057 | 5.6 |
| .00302 | .0131 | .0029 | 4.6 |

¹ Cooper and Mason: loc. cit.

In this experiment it is possible that the adsorption of the acidic ion is being measured as well as that of the hydroxylamine. The uptake in fact is greater than that observed when the hydroxylamine was directly estimated by Raschig's method (Table VII), although the general relationship of adsorption to concentration is the same in the two cases.

TABLE VII

| Initial conc. of $\text{NH}_2\text{OH.HCl}$ per cc. of water-phase | Amount of $\text{NH}_2\text{OH.HCl}$ taken up by 1 gm. protein A | Final conc. of $\text{NH}_2\text{OH.HCl}$ per cc. of water-phase B | Ratio A/B |
|--------------------------------------------------------------------|---------------------------------------------------------------------|-----------------------------------------------------------------------|--------------|
| .0297 gm. } .0121 } | Negative adsorption | | |
| .0078 | .0000 | .0078 | 0.0 |
| .00584 | .0044 | .0058 | 0.77 |
| .00293 | .0026 | .0029 | 0.90 |

The type of distribution is quite different from that obtaining with the foregoing phenols, acids, and amines. In the case of hydroxylamine hydrochloride the amount taken up by the albumin at first slightly increases with ascending concentration, reaching a maximum, and with further concentration rise the uptake diminishes to zero. In experiment 2 (Table VII) at the highest concentrations negative adsorption was actually observed. Similar results were obtained by Cooper and Nicholas¹ in the distribution of acetone between water and proteins. In the case of acetone a chemical explanation of the phenomena is improbable as the ketone only reacts slightly and with extreme slowness with amino-acids.²

In the course of the study of the uptake of phenols, acids, and bases, by proteins, four types of distribution have thus been observed.

- (1) Simple partition or solution, e.g. phenol, resorcinol.
- (2) Adsorption, e.g. picric acid, ethylamine.
- (3) Negative adsorption, e.g. hydrazine hydrate.
- (4) Maximum uptake at low concentrations, e.g. hydroxylamine hydrochloride.

VII. Correlation of the Results with Observations on Germicidal Power

In the following table the distribution-ratios of the foregoing and other substances between proteins and water are coordinated with their germicidal and inhibitory powers.

¹ Cooper and Nicholas: *Biochem. J.*, 19, 533 (1925).

² Cooper and Mason: *loc. cit.*

| Substance | Protein Water | | Germicidal concn. | Inhibitory concn. |
|--------------------------|-------------------------------------|------------------------------------------------|----------------------|----------------------|
| | Protein in colloidal solution | Protein in insoluble state (or pptd.) | | |
| Phenol | 3.0 | 12.0 | 1 in 130 | 1 in 550 |
| m-Cresol | 3.0 | 18.0 | 1 in 300 | 1 in 1150 |
| *o-chlorphenol | 3.2 | 28.8 | 1 in 440 | 1 in 2430 |
| p-chlorophenol | 4.2 | 36.0 | 1 in 650 | 1 in 4260 |
| Resorcinol | 4.0 | 4.0 | 1 in 40 | 1 in 350 |
| Pieric acid | — | 27.4-922 | 1 in 900 | 1 in 750 |
| Salicylsulphonic acid | 5.9-30.8 | 3.5-5.0 | — | 1 in 300 |
| Ethylamine | 1.2-6.8 | — | 1 in 170 | 1 in 1300 |
| Aniline | 1.2-5.7 | — | 1 in 70 | 1 in 225 |
| Hydrazine hydrate | Negative adsorption | — | 1 in 150 | 1 in 13,000 |
| Hydroxylamine HCl. | 0-5.6 | — | — | 1 in 9,000 |

* Cooper and Woodhouse: *Biochem J.*, 17, 600 (1923).

Conclusions

The general outcome of these comparative results is that the germicidal or inhibitory power of a substance bears no definite relationship to its solubility in or adsorption by proteins in colloidal solution, i.e. their natural state in the cell. Thus p-chlorphenol is 5 to 7 times as active as phenol in bactericidal power, yet it is only slightly more soluble than phenol in dissolved proteins. Salicylsulphonic acid on the other hand is adsorbed in considerable amount by proteins in colloidal solution, yet as a disinfectant it is less active than phenol. Other examples illustrating this point are brought out by a consideration of the tabulated results. Evidently germicidal and inhibitory power are not fundamentally determined by the capacity of the disinfectant to be dissolved or adsorbed by proteins in the *natural state of colloidal solution*.

When, however, we consider the results obtained with proteins in the *precipitated or insoluble condition*, it is found that a general parallelism between bactericidal action and solubility or adsorption exists. For example, pieric acid and the chlorphenols have a much higher distribution ratio than phenol, and they are also consistently more efficacious as disinfectants. Resorcinol and salicylsulphonic acid, on the other hand, are less active than phenols, and are also dissolved or adsorbed by proteins to a less degree. Now proteins occur naturally in living organisms in the condition of colloidal solution, and it is remarkable that the relations of disinfectants to proteins appear to correspond with bactericidal power only when proteins are in the precipitated state, i.e. an artificial form. The physicochemical relationships of disinfectants and poisons to proteins in the *insoluble condition* (denatured or un-

denatured), thus appear to have considerable bearing on the problem of the mechanism of their action on living organisms. The question as to why certain substances apparently *dissolve* in proteins, whilst others are *adsorbed* requires further consideration. It is probably incorrect to isolate the two phenomena. It is more likely that the processes of solution and adsorption are going on concurrently. With certain substances e.g. phenol, the formation of a solution in the protein phase predominates over adsorption; consequently the distribution follows the partition-law. In the case of other substances, e.g. picric acid, the surface factor of adsorption exceeds that of solution, and the distribution-ratio therefore varies with the concentration. The ratio varies in fact from 27-922, and this extraordinary deviation from the partition law shows that actual solution of picric acid in the protein phase must be negligible, the adsorption being almost entirely a surface concentration. It would thus appear that in the disinfection by phenol the first essential stage is the formation of a *solution* of this disinfectant in the bacterial proteins, and this is followed by the specific denaturing action of phenol on the colloidal structure of the cell. When picric acid acts as a disinfectant, however, it would seem that the preliminary process consists in its *adsorption* or concentration at the surface of the colloidal protoplasmic particles of the organism, as distinguished from the formation of a homogeneous solution.

The authors desire to express their thanks to the Department of Scientific and Industrial Research for a maintenance grant which has enabled this investigation to be carried out.

*Chemical Department,
University of Birmingham,
February 3, 1928.*

THE RATE OF ABSORPTION OF WATER BY BAKELITE

BY H. GENEVA LEOPOLD AND JOHN JOHNSTON

In a paper dealing with the rate of absorption of water by rubber Andrews and Johnston¹ showed that the observations on a series of sheets of different thickness of the same rubber compound follow practically a single curve² when the fractional saturation of the sheet as a whole—as determined by the increase in weight on immersion—is plotted against t/a^2 , t being the period of immersion in water, and a the half-thickness of the sheet. It was recognized that rubber is not the ideal substance for such a test of the general theory which leads to this conclusion, because of the oxidative and other changes which it might well undergo during the long period of immersion necessary; so we looked round for other materials, readily obtainable in uniform sheets of different thickness, which would be more stable under the conditions of experiment, and concluded to try cellulose acetate, celluloid and clear Bakelite (yellow and brown).³ We found however that the sheets of cellulose acetate reach substantial saturation in a few minutes, so rapidly indeed that a very thin sheet would promise to be useful as the absorptive member in a hygrometer; further that the celluloid sheets yielded in time to the water in which they were immersed so much of the original solvent or of camphor that conclusions based upon change of weight of the immersed sheets would be quite meaningless. The sheets of yellow Bakelite (presumably therefore those which in the course of manufacture were cured at a lower temperature or for a shorter time) upon immersion increased in weight for about two days, but thereafter lost steadily for upwards of two years, the final weight being about 1% less than the original dry weight; corresponding to this, phenol diffused out into the water and was easily recognisable. There remained therefore as satisfactory material for our purpose only the brown Bakelite, sheets of which showed a regular increase of weight throughout the period of immersion; but even with this material we found, when at the conclusion of the experiments the sheets were dried for three days at 110° (by which time the weight had become practically constant), that the final dry weight was less than the original weight by an amount averaging about 1%. This difference may be due, in part or wholly, to the fact that the samples were not so thoroughly dried before the initial weighing; to this loss of material of the sheets may be attributed the fact that the points for the thicker sheets corresponding to the very longest periods of immersion lie slightly below the

¹ Andrews and Johnston: *J. Am. Chem. Soc.*, 46, 640 (1924); see also Boggs and Blake: *Ind. Eng. Chem.*, 18, 224 (1926); Lowry and Kohman: *J. Phys. Chem.*, 31, 23 (1927).

² Immediately after immersion, and until the water, entering from either surface of the sheet, reaches its central plane, the rate of absorption is, of course, dependent on the area but not upon the thickness of the sheet.

³ For sheets of these materials we are indebted to the Eastman Kodak Company, the DuPont Company, and the Bakelite Company respectively.

curve. In any case, this difference was not taken into account in defining the increase of weight as a measure of the amount of water absorbed; and consequently the amount recorded as absorbed is rather below than above the true value.

The sheets used were 3×1 inch in three thicknesses, about 0.04, 0.07 and 0.14 inch respectively; they were dried ordinarily, weighed and immersed separately in distilled water in a stoppered bottle. At intervals the samples were removed, wiped with a piece of old linen in a standard way, transferred to a stoppered weighing bottle and weighed; they were then immediately re-immersed in distilled water. The increase of weight of three or four sheets of each thickness was observed in this way, and the results for each thickness agreed very closely; it suffices therefore to tabulate the data for one sheet of each thickness, as is done in Table I, Q being the percentage increase over the original dry weight of the sample. It may be mentioned that the thickness of the samples after soaking checked with the original within 1 or 2 mils (1 mil = 0.001 inch).

TABLE I
The percentage increase in weight (Q) of sheets of brown Bakelite 2a mils thick immersed in distilled water for t days

| A | | | B | | | C | | |
|-----------------------|------|-------|-----------------------|------|-------|----------------------|------|-------|
| 2a = 42 mils | | | 2a = 71 mils | | | 2a = 139 mils | | |
| orig. wt. = 2.4904 g. | | | orig. wt. = 4.6235 g. | | | orig wt. = 8.7850 g. | | |
| t | Q | Q' | t | Q | Q' | t | Q | Q' |
| days | obs. | curve | days | obs. | curve | days | obs. | curve |
| 0.7 | 0.25 | 0.18 | 2 | 0.27 | 0.18 | 1 | 0.09 | 0.06 |
| 1.7 | .39 | .33 | 7 | .52 | .48 | 2 | .14 | .10 |
| 5.7 | .61 | .72 | 10 | .57 | .58 | 6 | .22 | .17 |
| 7.7 | .75 | .83 | 14 | .75 | .67 | 8 | .24 | .19 |
| 13 | .92 | 1.03 | 18 | .83 | .74 | 10 | .27 | .26 |
| 15 | 1.16 | 1.10 | 32 | 1.02 | .99 | 13 | .31 | .29 |
| 19 | 1.29 | 1.28 | 35 | 1.06 | 1.02 | 16 | .33 | .31 |
| 26 | 1.48 | 1.48 | 42 | 1.09 | 1.09 | 20 | .37 | .37 |
| 33 | 1.66 | 1.68 | 56 | 1.29 | 1.27 | 24 | .42 | .42 |
| 40 | 1.87 | 1.85 | 85 | 1.52 | 1.56 | 27 | .45 | .45 |
| 54 | 2.23 | 2.18 | 187 | 2.36 | 2.42 | 34 | .48 | .54 |
| 69 | 2.54 | 2.50 | 210 | 2.46 | 2.57 | 48 | .58 | .62 |
| 98 | 2.99 | 3.00 | 246 | 2.66 | 2.79 | 62 | .66 | .72 |
| 200 | 4.18 | 4.12 | 341 | 3.24 | 3.27 | 91 | .79 | .86 |
| 223 | 4.34 | 4.30 | 451 | 3.68 | 3.73 | 193 | 1.14 | 1.20 |
| 354 | 5.16 | 5.08 | 539 | 3.96 | 4.02 | 216 | 1.20 | 1.27 |
| 382 | 5.18 | 5.17 | 568 | 4.06 | 4.10 | 252 | 1.31 | 1.37 |
| 464 | 5.40 | 5.39 | 845 | 4.94 | 4.78 | 458 | 1.80 | 1.87 |
| 552 | 5.56 | 5.60 | | | | 545 | 1.98 | 2.07 |
| 876 | 6.02 | 6.00 | | | | 574 | 2.04 | 2.13 |
| | | | | | | 851 | 2.86 | 2.66 |

After 28 months immersion each of the thinnest samples had increased $6.00 \pm 0.02\%$ in weight; it may be that they were still gaining weight very slowly, but we have assumed that 6.0% represents substantially the saturation value Q_s of this type of Bakelite. When the observed value Q , or the relative saturation Q/Q_s , is plotted against t/a^2 (t is number of days immersion, a is the half-thickness of the sheet), the points for all the sheets lie, with very few exceptions, very close to a *single* curve, so close that, on a diagram of the size which can be printed here, they would be indistinguishable from the curve. Consequently we show the degree of agreement of the results in Table I with this curve by presenting in the column Q' values interpolated at the designated values of t , or rather of t/a^2 , from the curve drawn on a large scale. This agreement is all that could be expected under the circumstances.

The advantage of this way of expressing the results is that one may from the curve predict for thick sheets the relative state of saturation, and thus avoid the necessity of continuing the experiments over long periods of years. This may be done from the following rounded values of t/a^2 (in days per square mil) corresponding to even arguments of the fractional saturation Q'/Q_s :

| | | | | | | | | | | |
|----------|------|------|------|------|------|------|------|------|------|------|
| Q'/Q_s | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1.0 |
| t/a^2 | 0.01 | 0.04 | 0.09 | 0.15 | 0.22 | 0.33 | 0.48 | 0.68 | 1.07 | 1.98 |

From this one may predict that the 140-mil sheets would not be essentially saturated until they had been immersed some twenty-six years! From these results it is clear that the rate of penetration of water into this type of Bakelite is so very slow that under all ordinary atmospheric conditions the amount of water absorbed would be negligible; this is doubtless a factor in the quality of this material as an electrical insulator.

From these experiments alone little can be said as to the mechanism of this water absorption; but there is no reason to believe that it differs essentially from the absorption of water by rubber. In this case, as the result of very careful and extensive investigation, Lowry and Kohman conclude that the process is essentially one of solution of water in the rubber, the end result being influenced by the presence of water-soluble impurities in the rubber, and by its rigidity which determines the ease with which the rubber sheet may swell and so provide space for the entering water.

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THE SURFACE LAYER OF LIQUIDS AND THE SIZE OF MOLECULES

BY SERGIUS G. MOKRUSHIN

The following equation connecting the latent heat of evaporation, λ , with the surface tension, σ was deduced by W. Ostwald¹

$$\lambda/2 = \sigma\Omega \quad (1)$$

where Ω is the area of the liquid surface. It follows from this equation that the surface energy of molecules lying in the interface liquid-vapour is half of their latent heat of evaporation. The value of Ω for one molecule in the surface layer is calculated by Ostwald on the assumptions, apparently, that (a) each molecule is a cube, the cubes being as closely packed as possible, and (b) that the volume of a molecule in the liquid state is M/d where M is the molecular weight in the vapour state, and d is the density of the liquid. The length of a cube edge, t , can readily be calculated, for

$$M/d = \Omega t \quad (2)$$

$$\text{and hence } t = 2\sigma M/\lambda d \quad (3)$$

which equation is employed by Ostwald for the calculation of the "diameter" (Durchmesser) of a molecule.

We will now examine more closely equations (1) and (2) from which (3) is derived. In (1) the surface energy of a molecule in the surface layer is $\lambda/2$, which implies that when, on evaporation, the molecule is removed from the surface it acquires an additional amount of energy, $\lambda/2$. After evaporation therefore $\sigma\Omega$ equals half the surface energy of the molecule, the whole surface of which is now free. But the surface energy of molecules will be half of their surface energy when in the vapour state only if the surface of the liquid consists of spherical or ellipsoidal molecules in contact, or of polyhedra symmetrically disposed, and with the edges, not the faces, in contact. It seems most probable that surface layer molecules are spherical or ellipsoidal as has been previously suggested by the writer in a paper² where the molecular surface energy was regarded as equal to the internal latent heat of evaporation, λ_1 , viz.,

$$\lambda_1 = S\sigma \quad (4)$$

where $S = N\pi d^2 =$ the molecular surface in the vapour state, N being the Avogadro number, and d the molecular diameter. "Diameters" calculated by (4) do not agree well with those calculated from (3) by Herz³, Walden,⁴ and others, but approach more closely to those determined by Sirk⁵ on the basis of Debye's work. Another objection to Ostwald's equation is the replacement of Ω by M/d , for which no adequate grounds appear, and which entails no interspaces between molecules. This can be the case only when

molecules are in the form of cubes, hexahedra, honeycombs, etc., and not of spheres. In the simplest case, that of the cubical form, equation (1) cannot hold because the surface energies of closely packed cubical molecules at the surface of the liquid will be only one-sixth and not one-half of those in the vapour state, as only one face of each cube in the surface layer is free. Hence the values of t are three times as great as those derived from equation (3), i.e. are nearer to those derived from (4).

Ostwald suffered from lack of data concerning the shape of molecules and the structure of surface layers of liquids. It is only comparatively recently that Langmuir's⁶ investigations have led to a more or less clear insight into the structure of such layers, the conclusions attained not being in harmony with van der Waals'⁷ assumption of a continuous change of vapour to liquid and of a non-abrupt liquid-vapour interface. At present the surface layer is considered to be unimolecular, forming a definite liquid-vapour interface. (See Brillouin⁸). The writer⁹ has shown that molecules of liquid at the boiling point have the structure of a honeycomb cell and are in a contracted state, but in the surface layer they must be approximately spherical as the attractive forces of the lower molecules in the liquid are not fully experienced. It follows that the density of the surface layer is less than that of the bulk liquid. Raman¹⁰ has lately arrived at the same conclusion from investigations of the scattering of light at liquid surfaces, but explains the phenomenon on the hypothesis of Brownian movement of the molecules, that is the molecules are not in contact. The writer, however, is in agreement with Langmuir¹¹ that the surface layer molecules are in contact, and ascribes the decrease in density as due to expansion.

Published values, obtained by independent methods, of the diameters of such molecules also support the writer's assumptions. Values for water, for example, are (a) 5.5 Å, Langmuir,¹² from determinations of the negative adsorption of potassium chloride, (b) 5.1 Å, Jaeger¹³, from the kinetic theory of gases and the capillary constant, (c) 5.0 Å, Raman, from his above mentioned experiments. These values are very close to that obtained by the writer² from equation (4), namely, 5.12 Å.

In conclusion, it seems necessary to direct attention to the apparent fact which emerges from Raschig's¹⁴ and Zelmsky's¹⁵ work on catalysis, that molecules may suffer a simultaneous change of volume and shape.

Summary

1. Fresh support is adduced for the author's assumptions concerning the structure of the surface layers of liquids, and for the correctness of his formula for calculating the diameters of molecules.

2. It is shown from theoretical consideration that the surface layer should have a smaller density than the main liquid.

3. Attention is directed to a possible type of deformation of molecules involving a simultaneous volume and shape change.

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REACTION VELOCITY AT A LIQUID-LIQUID INTERFACE

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Introduction. Very little work has been done upon the velocity of reaction in a heterogeneous system consisting of two non-miscible liquids, and those cases which have been studied are of the type in which at least one of the reactants is soluble in both liquid phases. In a reaction of this type, the reaction velocity depends upon the rate of diffusion of one or more of the reactants across the junction of the two phases, and is not due to surface phenomena.

It was therefore decided to investigate a reaction between two substances 'a' and 'b' in two non-miscible solvents 'A' and 'B,' 'a' being insoluble in 'B,' and 'b' being insoluble in 'A.' In a case of this kind, the reaction can only take place at the junction of the two phases, and will depend upon the formation of adsorbed surface films. In order to simplify matters, it was decided to use as one reactant a solution of an electrolyte in water, which gives only a slight negative adsorption, and as the other reactant a solution of non-electrolyte in a non-dissociating solvent which will give a positive adsorption. The reaction can then only take place by the ions of the electrolyte striking the adsorbed film of the non-electrolyte.

Although a reaction of this kind must be a true surface reaction, it is still possible that it may be influenced by the rate of diffusion of the non-electrolyte to the surface. This will be the case if the rate at which the adsorption equilibrium is adjusted is slow compared with the rate at which the molecules are removed from the surface layer by reaction. In this case the reaction velocity will be affected greatly by the rate at which the layer is stirred, while if the reaction velocity is only a function of the equilibrium condition of the adsorbed layer, the rate of stirring should have no influence. From the small difference which is found to exist between the static and dynamic surface tensions of solutions, it appears that the oriented monomolecular films formed in solutions are not disturbed by a moderate degree of stirring.

Choice of a reaction. The reaction to be examined should have the following characteristics:

(a). The two solvents must not be miscible to any great extent, and neither must be very volatile. Also they must not readily form an emulsion, and they must have specific gravities differing as far as possible so that the liquid to liquid interface shall not easily be deformed by stirring either of the layers.

(b). Each of the reacting substances must be insoluble in one phase and soluble in the other.

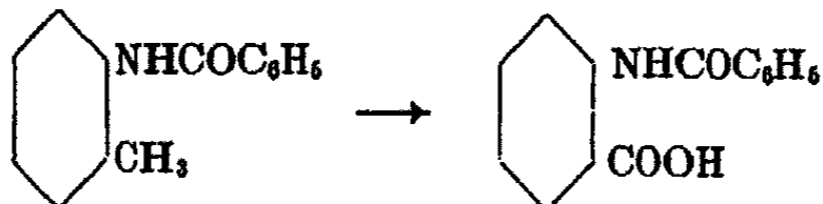
(c). The products of reaction must be soluble in at least one of the phases.

(d). The electrolyte must be a neutral salt, since hydrion and hydroxidion have a disturbing effect upon surface conditions.

(e). The reaction must proceed at a measurable velocity at ordinary temperatures.

(f). At least one of the reactants must be capable of accurate determination in solution.

The reaction finally chosen as suitable was the oxidation of benzoyl-*o*-toluidide in benzene solution to benzoyl-anthranilic acid, by a neutral aqueous solution of potassium permanganate, according to the equation:—



Each solvent was saturated with the other before use. Experiment showed that benzoyl-*o*-toluidide is quite insoluble in a saturated solution of benzene in water, and that potassium permanganate is quite insoluble in a saturated solution of water in benzene, the temperature in each case being about 25°C. The product of reaction, benzoyl-anthranilic acid, was found to be only slightly soluble in water, but since only initial velocities were measured and a large volume of water was present, in no experiments did it separate out.

The benzoyl-*o*-toluidide used was prepared by the Schotten-Baumann reaction from benzoyl chloride and pure *o*-toluidine. It was filtered, pressed, washed with dilute hydrochloric acid and water, and dried on the water-bath. One preparation was recrystallised from alcohol and another from benzene. After drying in a steam oven each preparation melted at 141°C, and a mixture of the two also melted at 141°C. Both were therefore considered pure and were used indifferently in the subsequent work.

Measurement of Reaction Velocity. The apparatus for measuring the reaction velocity is shown in Fig. 1. The glass jar 'A' was of about 5 litres capacity. The permanganate layer 'a' was stirred by the stirrer 'B,' and the benzene layer 'b' by the stirrer 'c.' The stirrers were of glass and were connected by pulleys so that 'B' rotated about four times as fast as 'c.' 'B' was enclosed by the outer tube 'D' so that it moved only in the permanganate solution.

The progress of the reaction was followed by titrating from time to time 10 ccs. of the permanganate layer which were withdrawn by a pipette attached to the rubber tubing at 'E.'

At the commencement of each run the permanganate solution, approximately at 25°C was run into the jar clamped in the thermostat. A known volume of benzene was then added, and left for half an hour to acquire the temperature of the thermostat. The reaction was started by adding a known volume of a benzene solution of benzoyl-*o*-toluidide, which had previously been brought to the temperature of the thermostat. These solutions were made up by dissolving a known weight of benzoyl-*o*-toluidide in a known volume of benzene.

Preliminary Experiments. Two runs were first made in which the solutions used were the same in each case, but the speed of stirring of the benzene

layer differed in the two cases. As a temporary standard for titrating the permanganate solution an acidified solution of ferrous ammonium sulphate was used. Since comparative values only were required, the strength of the solutions used was known only very approximately.

In the preliminary experiments, as in all measurements of reaction velocity, the following points were adhered to:—

(a). A large volume of permanganate solution was used, so that the removal of several 10 cc. portions should not affect the concentration to any considerable extent.

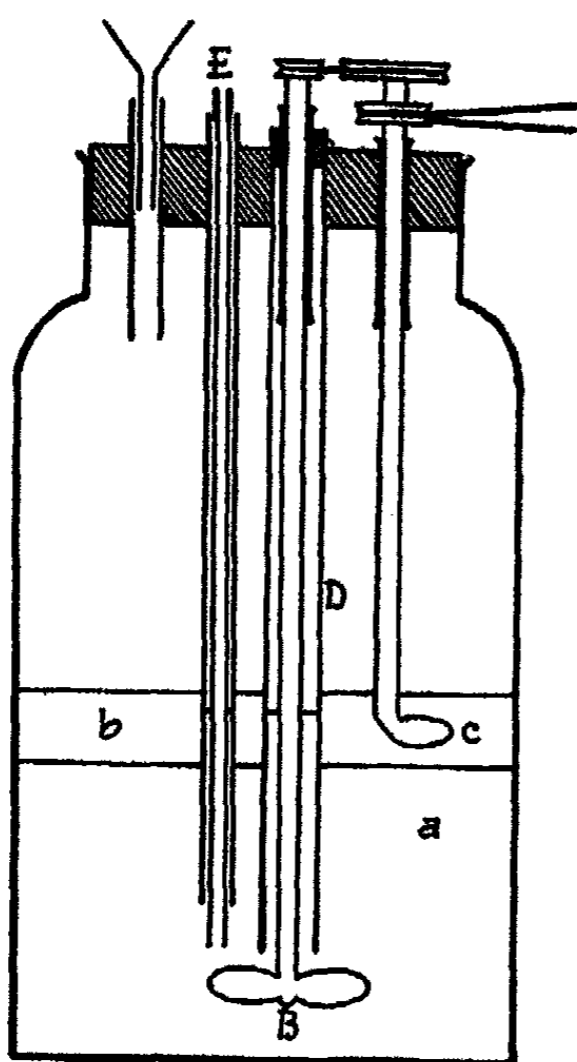


FIG. 1

(b). The benzoyl-o-toluidide was always present in large excess compared to the permanganate used up, so that the concentration of the former should not change materially during the initial stages of the reaction.

The results of the preliminary runs show that after a very short initial stage, the reaction attains a velocity which is not affected by increasing the rate of stirring four-fold. Thus with an initial titre in each case of 13.9 ccs. with the faster rate of stirring the titre changed from 12.35 ccs. to 11.40 ccs. in 1.5 hours, while the corresponding change at the slower rate of stirring was from 13.20 ccs. to 12.25 ccs. in the same time.

Titration of potassium permanganate. For further experiments a solution of sodium oxalate approximately N/100 was used for titrating the permanganate solutions.

In runs 1-4 inclusive, the 10 ccs. of permanganate solution was added to about 50 ccs. of hot, 50% sulphuric acid. 100 ccs. of boiling water was then added, and the solution often remained at 80°-90°C for some minutes before titration. In each of these runs very erratic results were obtained, although the general trend of the titres corresponded to the progress of the reaction. It was therefore thought that the method of titration was at fault, and after run 4 the permanganate layer (containing the products of reaction) was removed, and 10 cc. portions were titrated with standard sodium oxalate under different conditions. It was found that if the procedure described above was adopted, the titre decreased on standing, to the extent of about 1% in one minute. This accounts for the erratic points obtained. However, if the permanganate was added to cold sulphuric acid, then diluted with water, and warmed gradually to 70°C, the titre was not altered by keeping the solution

at 70°C for ten minutes. This procedure was therefore employed in all subsequent runs, and the results of runs 1-4 inclusive were not used.

A suggested explanation of the observed decrease in titre is that the benzoyl-anthranilic acid is partially hydrolysed to anthranilic acid by contact with hot 50% sulphuric acid. The free amino-group is then oxidised by a part of the permanganate, thus reducing the titre.

Experimental Results (First series). In this series of runs the temperature of the thermostat was $24.65^{\circ} \pm 0.01^{\circ}\text{C}$.

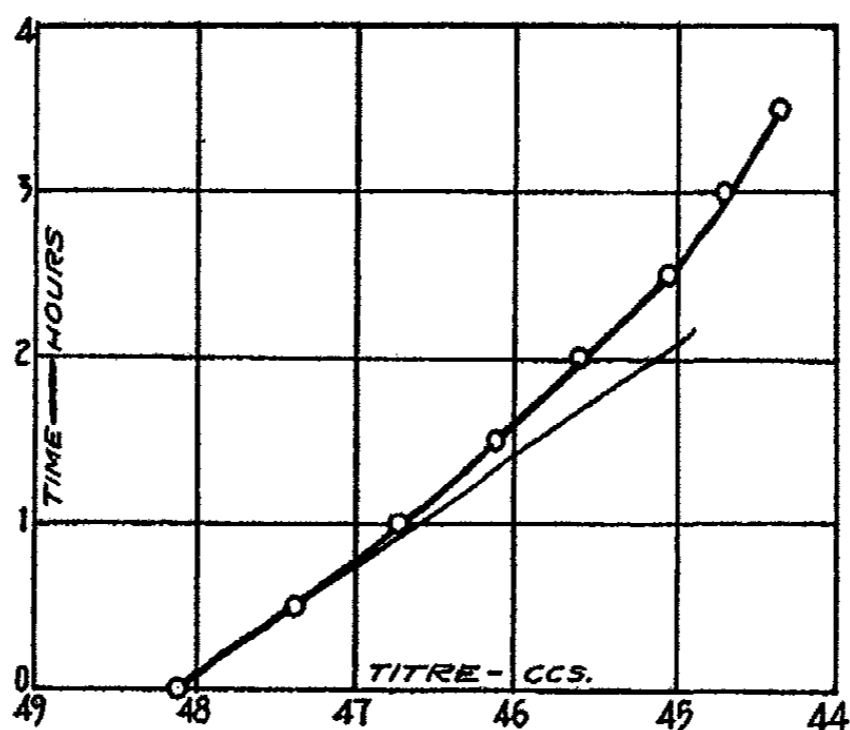


FIG. 2

In all, sixteen runs were taken. Besides the first four, run No. 6 was rejected because the stirrer was broken, and run No. 11 because for some unknown reason the titres are erratic.

In each run, on plotting the titres against the time it was found that the initial portion of the graph always approximates to a straight line, though in some cases the observed initial titre does not lie upon the line which passes through the subsequent points, indicating a short initial stage. In these cases the initial concentration is taken to be that corresponding to the first point on the straight line. The initial reaction velocity given in the tables of results is obtained graphically from the straight portion of the curve.

As an example, the full experimental figures for run No. 8 are given:—

Run (8). 1200 ccs. water
 400 ccs. KMnO_4 (A)
 250 ccs. benzene

Initial titre = 48.12 ccs. (oxalate B).

250 ccs. benzoyl-o-toluidide B added at 10.30.

| Time | Titre | Time | Titre |
|-------|-------|-------|-------|
| 10.30 | 48.12 | 12.30 | 45.60 |
| 11.0 | 47.33 | 1.0 | 45.60 |
| 11.30 | 46.73 | 1.30 | 44.70 |
| 12.0 | 46.11 | 2.0 | 44.34 |

The graph of this run is given in Fig. 2.

In every run the total volume of the aqueous layer was 1600 ccs., and the total volume of the benzene layer 500 ccs. In runs Nos. 5, 7 and 8 the concentration of the sodium oxalate used corresponded to 1.98×10^{-6} gram moles KMnO_4 per cc. In runs Nos. 10-16 inclusive the corresponding figure was 6.12×10^{-6} .

The results of the first series are summarised in the following table, in which:—

A = Initial concentration of KMnO_4 in oxalate titre per 10 ccs. of solution.

B = Concentration of benzoyl-o-toluidide in grams per litre.

R = Initial rate of reaction in ccs. oxalate solution per 10 ccs. permanganate solution per hour.

| Run | A | B | R |
|-----|-------|------|------|
| 5 | 36.14 | 4.55 | 0.82 |
| 7 | 24.86 | 4.55 | 0.53 |
| 8 | 48.12 | 4.55 | 1.15 |
| 10 | 26.19 | 3.94 | 2.70 |
| 12 | 26.60 | 2.95 | 1.52 |
| 13 | 26.52 | 8.69 | 3.68 |
| 14 | 25.40 | 5.94 | 3.55 |
| 15 | 24.63 | 2.14 | 0.65 |
| 16 | 26.34 | 4.96 | 3.50 |

In runs Nos. 5, 7 and 8, 'B' remains constant, while 'A' varies. These results can therefore be used to test the dependence of the reaction velocity upon the permanganate concentration. Expressing both the quantities in the units given in the table, we have the following values for the ratio R/A:—

$$\text{Run (5).} \quad 0.82/36.14 = 0.0227$$

$$\text{Run (7).} \quad 0.53/24.86 = 0.0214$$

$$\text{Run (8).} \quad 1.15/48.12 = 0.0223$$

The constancy of this ratio shows that the reaction is monomolecular with respect to potassium permanganate. This being so, we can correct for the variations in initial concentration of permanganate in runs 10-16. The following table contains the initial velocities corrected to a uniform initial concentration corresponding to a titre of 26.19 ccs. oxalate solution.

| Run | B | R' | Run | B | R' |
|-----|------|------|-----|------|------|
| 10 | 3.94 | 2.70 | 14 | 5.94 | 3.66 |
| 12 | 2.95 | 1.46 | 15 | 2.14 | 0.69 |
| 13 | 8.69 | 3.63 | 16 | 4.96 | 3.50 |

These figures are plotted in Fig. 3, which represents the dependence of the reaction velocity upon the concentration of the benzoyl-o-toluidide. It is seen that for concentrations above about 5-6 grams per litre, the value of R' becomes independent of that of B. This range of concentrations was therefore used in the second and third series of experiments undertaken to determine the temperature coefficient of the reaction velocity.

Experimental Results. (Second and third series). In the second series the temperature of the thermostat was 25.08°C., and in the third series it was 14.90°C. Three runs were carried out at each temperature, with concentrations of benzoyl-o-toluidide of approximately 6, 7 and 8 grams per litre. In both runs the oxalate solution used had a strength corresponding to 5.61×10^{-6} gram moles KMnO_4 per cc.

In each series it was found that by plotting the points of all three runs on one graph a straight line was obtained for the initial portion which passed through the points of each separate run, thus confirming the result of the first series namely, that for concentrations of benzoyl-o-toluidide above about 5-6

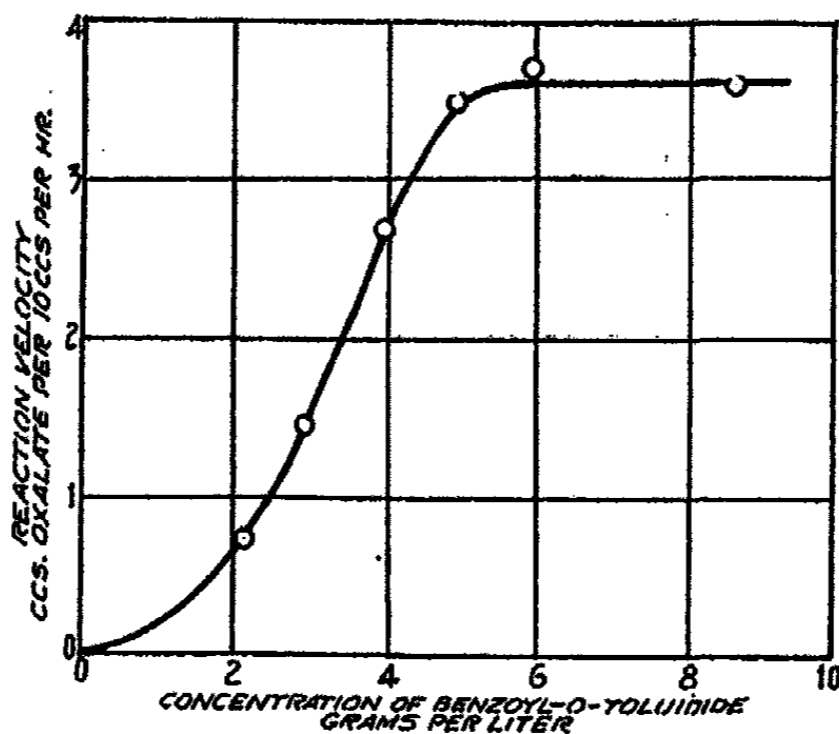


FIG. 3

grams per litre the reaction velocity is independent of the concentration. The reaction velocity in each series was determined by measuring the slope of the line. The results obtained were as follows:—

Series (2).

At 25.08°C with an initial titre of 16.65 ccs., the initial velocity was 3.60 ccs. per 10 ccs. per hour.

Series (3).

At 14.90°C with an initial titre of 17.15 ccs., the initial velocity was 0.28 ccs. per 10 ccs. per hour.

If we correct the second value for the small difference in initial titre, the values become 3.60 ccs. and 0.27 ccs. respectively.

Measurement of Surface Tension. In order to determine how the interfacial tension between the two layers varied with the concentration of benzoyl-o-toluidide, the drop-weight method was used. It was of course impossible to use permanganate solutions, but since these were dilute, the error involved in using water will be small, at least as regards the *variation* of the surface tension with concentration.

The apparatus used was a modification of that used by Harkins.¹ The tip was about 7 mm. in diameter and was selected to be truly circular. It was ground flat with carborundum powder and water, and finally polished with rouge. The time allowed for each drop to fall was at least three minutes, and under these circumstances the surface tension is proportional to the drop-weight. Since the density of the solutions used varied only from 0.8740 to 0.8755, the drop-volume can in this case be taken as a measure of the surface tension.

The results obtained are given in the following table in which:—

c = concentration of benzoyl-*o*-toluidide in grams per litre.

v = volume of one drop of water in ccs.

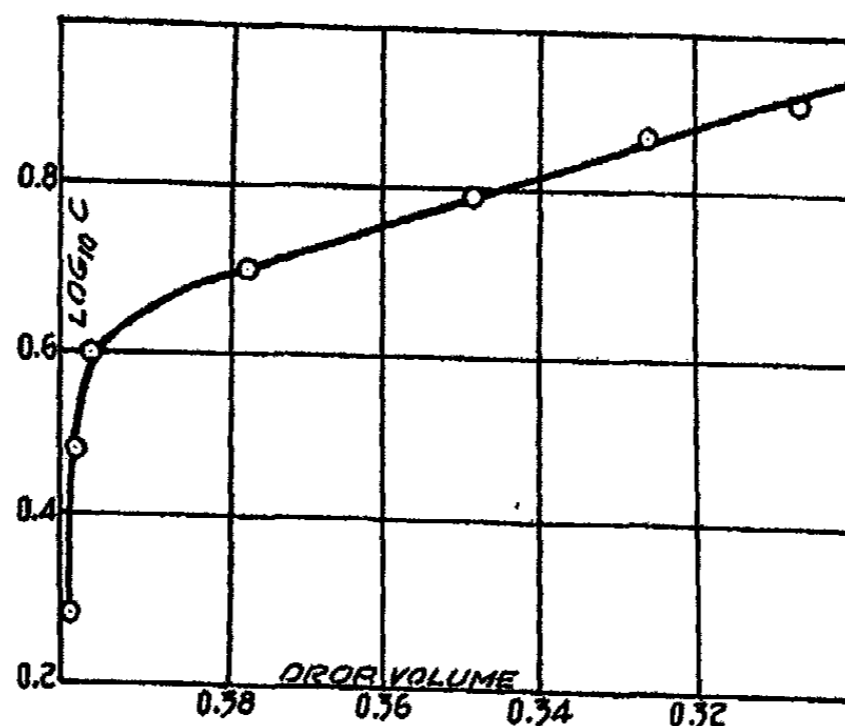


FIG. 4

Both the water and the benzene solutions were saturated with respect to each other by shaking in the thermostat before measuring the drop-weight. All the surface tension measurements were carried out in the thermostat at 24.65°C.

| c | $\log_{10} c$ | v | c | $\log_{10} c$ | v |
|------|---------------|-------|------|---------------|-------|
| 1.94 | 0.288 | 0.398 | 5.02 | 0.701 | 0.377 |
| 2.98 | 0.474 | 0.398 | 7.32 | 0.865 | 0.326 |
| 4.02 | 0.604 | 0.396 | 8.04 | 0.905 | 0.314 |
| 6.19 | 0.792 | 0.348 | | | |

The variation of the surface tension with the concentration is shown in Fig. 4, in which the drop-volume is plotted against $\log_{10} C$.

Discussion of results. In the introduction the theory was advanced that reaction took place by permanganate ions striking an adsorbed surface of benzoyl-*o*-toluidide molecules. In this case the reaction velocity at a given temperature depends only upon the nature of the surface layer, and upon the

¹ Harkins, etc.: J. Am. Chem. Soc., 38, 228, 252 (1916).

rate of impact of the permanganate ions. The hypothesis is supported by the following experimental facts:—

(a). The preliminary experiments show that the reaction velocity is independent of the rate of stirring, and hence not dependent on the rate of diffusion of either reactant towards the interface.

(b). The results of runs 5, 7 and 8 in the first series of velocity determinations show that the velocity is directly proportional to the concentration of potassium permanganate, i.e., since the solutions are dilute, to the rate at which the permanganate ions strike the surface.

(c). The reaction velocity is found to have a large temperature coefficient, increasing about 13-fold for a rise of 10°C. This shows an analogy to heterogeneous gas-reactions, in contradistinction to diffusion reactions, for which the temperature coefficient is very small.

This being the case, it should be possible to observe a connection between the reaction velocity and the condition of the surface film.

The fundamental equation for the extent to which adsorption at an interface takes place is the Gibbs-Helmholtz equation:—

$$\Gamma = - \frac{1}{RT} \frac{\partial \sigma}{\partial \ln c}$$

where c = concentration of dissolved substance.

σ = surface tension.

Γ = increase of concentration at the interface in moles per sq. cm.

The direct confirmation of this value for the excess concentration offers great experimental difficulties. A fair agreement between calculated and observed values was obtained for the liquid-gas interface by Donnan and Barker,¹ and by Frumkin,² but the results of W. C. McC. Lewis³ on the liquid-liquid interface are not so satisfactory.

Indirect confirmation has however been obtained by several workers. It is found in general that for solutions of non-electrolytes $\partial \sigma / \partial \ln c$ becomes constant above a certain limiting value of c . This means that Γ has reached its maximum possible value, i.e. that the surface is completely covered. Values for the molecular diameter are calculated from the value of Γ and good agreement is found with values obtained by other methods or for other solvents.

The present work gives another opportunity of testing the same point. It is seen from Fig. 3 that $\partial \sigma / \partial \ln c$ becomes constant for all concentrations above about 5–6 grams per litre. It would therefore be expected that 'ceteris paribus,' the reaction velocity would be the same for all benzoyl-o-toluidide solutions having concentrations above this limit. The curve in Fig. 3 be-

¹ Donnan and Barker: Proc. Roy. Soc., 85A, 557 (1911).

² Frumkin: Z. physik. Chem., 115, 253 (1925).

³ Lewis: Phil. Mag., 15, 499 (1908); 17, 466 (1909); Z. physik. Chem., 73, 129 (1910).

comes parallel to the concentration axis for high concentrations, the point of inflection lying between 5 and 6 grams per litre, so that the dependence of the reaction velocity on the condition of the surface film is confirmed by experiment. The constancy of the reaction velocity at high concentrations is shown not only by Fig. 3, but by the agreement of the separate runs in series (2) and (3).

The present experiments therefore provide an independent verification of the presence of a saturated monomolecular adsorbed layer at the surface of a concentrated solution of a non-electrolyte. It is suggested that this work can be extended to a general study of adsorption by other kinetic properties of interfaces, e.g., rates of evaporation. Such experiments are now in progress.

For concentrations of benzoyl-o-toluidide corresponding to a complete covering of the surface, it is of interest to compare the number of permanganate ions reduced with the total number which strike the surface. This latter number can only be calculated if we assume that the permanganate layer is homogeneous throughout, and neglect the surface film of water molecules.¹ Making these somewhat doubtful assumptions, we have by the kinetic theory²—

$$n = \frac{W}{\Phi_b} \cdot \frac{\bar{c}}{\sqrt{6\pi}} \quad (6)$$

where n = number of ions per second striking a given unit area.
 W = number of ions contained in a total of N species (ions + solvent molecules).

\bar{c} = root-mean-square velocity of an ion.

Φ_b = molecular co-volume of solution.

Since the solutions are dilute we can write:—

$$W = cN\Phi_b$$

where c = concentration in gram moles per cc.
 and hence:—

$$X = \frac{3600 c A \bar{c}}{\sqrt{6\pi}}$$

where X = reaction velocity in gram moles per hour.
 A = area of interface.

In the second series of velocity determinations the initial titre was 16.65 ccs. This corresponds to a concentration of:—

$$\begin{aligned} c &= 16.65 \times 5.61 \times 10^{-6} \times \frac{1}{10} \\ &= 9.37 \times 10^{-6} \text{ gram moles MnO}_4' \text{ per cc.} \end{aligned}$$

¹ Morgan and Egloff: *J. Am. Chem. Soc.*, 38, 844 (1916); Harkins: 39, 1848 (1917); 47, 1610 (1925); King: *Kansas Exp. Sta. Tech. Bull.*, 9 (1922); Mathews and Stamm: *J. Am. Chem. Soc.*, 46, 1071 (1924).

² See Traube: *Wied. Ann.*, 61, 380 (1897); also Dieterici: 66, 826 (1898). Compare the equation used by Langmuir for gases. *Trans. Faraday Soc.*, 1922.

From the kinetic energy of the MnO_4^- ion at 25°C . we obtain,

$$\bar{c} = 2.45 \times 10^4$$

$$A = 132 \text{ sq. cm.}$$

$$\text{Hence } X = \frac{3600 \times 0.37 \times 10^{-4} \times 132 \times 2.45 \times 10^4}{\sqrt{6} \times 3.14}$$

$$= 2.51 \times 10^4 \text{ gram moles KMnO}_4 \text{ per hour.}$$

The initial velocity determined experimentally was 3.60 ccs. oxalate per 10 ccs. solution per hour. Since the total volume of solution was 1600 ccs., we have:—

$$X = 3.60 \times 160 \times 5.61 \times 10^{-6}$$

$$= 3.22 \times 10^{-3} \text{ gram moles KMnO}_4 \text{ per hour.}$$

There is thus a ratio of about $1 : 10^{-7}$ between the number of MnO_4^- ions which reach the surface layer and the number which react with benzoyl-*o*-toluidide at 25°C .

There are two factors which may account for this large number of unfruitful collisions:—

(a). That only collisions possessing an energy of impact greater than a limiting value 'E' are fruitful. If the adsorbed layer can be regarded as entirely stable, then 'E' refers only to the energy of the permanganate ion. Probably, however, the adsorbed toluidide molecules are in varying states of vibration and strain, in which case 'E' refers to the joint energy of the two colliding molecules.

(b). That certain 'phase conditions,' e.g. mutual orientation of the reacting molecules, are necessary to reaction.

That the first of these factors is present seems certain on account of the very small number of fruitful collisions, and more especially on account of the high temperature coefficient. The second factor may or may not be effective simultaneously with the first.

If we consider it as a case of simple thermal activation the variation of the reaction velocity with the temperature over a fairly small temperature range is given by:—

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$

where the 'energy of activation,' E, is a constant. In the present instance, measurements have only been made at two temperatures, so that it is impossible to show that the $\ln k - 1/T^2$ graph is a straight line, i.e. that E is actually constant. However if we assume its constancy, a value can be calculated from the temperature coefficient.

Taking the mean temperature as 20°C .,

$$\frac{\ln_{10} 3.6 - \ln_{10} 0.28}{10} = \frac{E}{2 \times 293^2}$$

$$E = \frac{2 \times 293^2 (\log_{10} 3.6 - \log_{10} 0.28)}{4.343}$$

$$= 43,700 \text{ calories}$$

Assuming that the calculation of the total number of collisions is correct, we have:—

$$\frac{\text{Effective collisions}}{\text{Total collisions}} = 1.28 \times 10^{-7}$$

from which we can calculate a value for E according to the Maxwell distribution law,

$$\frac{\text{Effective collisions}}{\text{Total collisions}} = e^{-E/RT}$$

$$\text{whence } 1.28 \times 10^{-7} = e^{-\frac{E}{2 \times 298}}$$

$$\begin{aligned} E &= 2 \times 298 \times 15.87 \\ &= 9,500 \text{ cal.} \end{aligned}$$

Thus the two values of E , 43,700 cal. and 9,500 cal. calculated on the basis of simple thermal activation are very different, and the discrepancy will be increased if a phase factor (necessarily less than unity) is present. It seems probable that although the equation used to calculate the total number of impacts may be approximately correct for an imaginary plane in the interior of the solution, it will fail entirely at a phase interface on account of the adsorbed water layer at the surface and the electrical action. In any case, reliance cannot be placed upon the value 43,700 cal., depending as it does on a single determination, and the application of simple kinetic theory to an ionic solution cannot give more than very approximate results.

Thus in this case the results of thermal calculations are inconclusive. It appears, however, that a study of this type of reaction may prove useful in the study of thermal activation. In the ordinary heterogeneous gas-reaction, the surface is not readily reproducible, nor is its area easily measured, while in the homogeneous bimolecular gas-reaction the calculation of the total number of collisions depends on molecular diameters, which are not known accurately. In a reaction of the present type, the collisions are between moving molecules and a well-defined interface, and their number can be calculated by simple kinetic theory. It would seem that the complications met with in the present work might be obviated by the study of a reaction at a gas-liquid surface.

Summary

(1). The velocity of the surface reaction between benzoyl-*o*-toluidide in benzene solution and potassium permanganate in aqueous solution has been determined for varying concentrations of the two reactants and at temperatures of 15°C and 25°C.

(2). Comparative measurements of the interfacial tension between water and benzene solutions of benzoyl-*o*-toluidide have been carried out by the drop-weight method.

(3). It has been shown that the above reaction is caused by permanganate ions striking an adsorbed layer of benzoyl-o-toluidide, and that its velocity is not dependent upon diffusion from one solvent to another.

(4). Comparison of the velocity curves with the surface tension has afforded an independent confirmation of the Gibbs-Helmholtz adsorption equation.

(5). Calculations have been made to test the hypothesis of thermal activation for this reaction, but with inconclusive results.

(6). It is suggested that more conclusive results might be obtained by the study of a reaction at the gas-liquid interface, and that the general problem of inter-phase kinetics may provide a valuable line of approach in the study of adsorption.

In conclusion, the author wishes to express his gratitude to Sir Harold B. Hartley for his advice, encouragement and assistance throughout the work.

*Physical Chemistry Laboratories,
Balliol and Trinity Colleges,
Oxford.
December 29, 1927.*

THE OPTICAL ACTIVITY AND COLLOIDAL BEHAVIOR OF AQUEOUS GELATIN DISPERSIONS*

BY ELMER O. KRAEMER AND J. R. FANSELOW**

In a preliminary study the authors¹ observed that the influence of temperature and pH upon the optical activity of aqueous gelatin systems does not resemble that usually found with solutions containing optically active acids, bases, or salts. The optical behavior of solutions of tartaric, malic, and other acids or their salts² may be rather simply coordinated with the ordinary dissociation constants and the extent of salt formation or hydrolysis. To each of the various ionic and molecular species in solution may be assigned a characteristic rotatory power so that the net rotatory power of solutions of varying composition is given by simple additive processes. In gelatin systems, on the other hand, the relationship between rotatory power and composition is not only more complicated than acid or base combination curves would suggest, but it appears also to be masked by other influences. Much more apparent is a parallelism between gel formation and optical activity which indicates that the rotatory power of gelatin systems may be controlled by colloidal features, such as degree and state of dispersion, as well as by intramolecular stereochemical relations in the usual sense. In the light of these results³ certain criticisms were raised against various hypotheses involving tautomeric equilibria which have been proposed to explain the physical behavior of gelatin systems.⁴

The continuation of the investigation has shown the relationship between rotatory power and colloidal behavior to be an intimate and detailed one. Above 30° to 40°C, depending upon the concentration, aqueous gelatin dispersions behave very much like ordinary solutions. The light-scattering capacity, resistance to shear (or apparent viscosity), and the optical activity show no striking change with change in pH or temperature. The Tyndall intensity and the relative viscosity are both rather small; the latter at least approximately obeys Poiseuille's equation. Both relative viscosity and opti-

* Presented in part at the A.C.S. Regional Meeting, Madison, Wis., May 1926, and the Fourth Colloid Symposium, Mass. Inst. of Technol., 1926.

** This paper constitutes a portion of the doctorate thesis submitted by J. R. Fanselow to the University of Wisconsin.

¹ Kraemer and Fanselow: *J. Phys. Chem.*, 29, 1169 (1925).

² Vellinger et al: *Compt. rend.*, 180, 742 (1925); 182, 1625; 183, 741 (1926); 184, 94 (1927); *Arch. phys. biol.*, 5, 42 (1926); *Bull. soc. chim.*, 37, 841 (1925); Liquier: *Compt. rend.*, 180, 1917 (1925); 183, 195 (1926); *Bull. soc. chim. Belg.*, 34, 459 (1926); *Ann. phys.*, 8, 121 (1927); Darmois: *Compt. rend.*, 182, 1211 (1926); 184, 1239, 1438 (1927); Levene et al: *J. Biol. Chem.*, 70, 243, 327 (1926); 72, 815 (1927).

³ Shortly before the appearance of the authors' preliminary paper, brief studies of the optical activity of gelatin systems were reported by Vlés and Vellinger (*Compt. rend.*, 180, 439 (1925)) and by Bogue and O'Connell (*J. Am. Chem. Soc.*, 47, 1694 (1925)). These studies were too brief, however, to give an adequate view of the optical behavior or to reveal its relation to gel formation.

⁴ These hypotheses are also discussed in *J. Phys. Chem.*, 29, 410 (1925); 31, 764 (1927).

cal activity present a poorly defined minimum value at a pH approximately 5. On either side the magnitude of these quantities rises and falls with those properties which are sometimes said to be controlled by Donnan membrane equilibrium effects. A suggestion of a minimum also occurs at pH ca. 1, and near 8.5. It is noteworthy that the specific rotation of gelatin under these conditions is so slightly modified by combination with acid or base.

At lower temperatures conditions are quite different. The Tyndall effect reveals regions of precipitation¹ at various pH's—particularly near pH 5 and 1. In such regions, for dilute gelatin systems, the optical activity and resistance to shear do not reach their maximum values, and the tendency to gel formation is low; *but just adjacent to such regions of precipitation are rather narrow regions with a pronounced tendency to gel formation and a striking increase in rotatory power.* The resistance to shear rises steeply, but is no longer independent of the rate of shear. In fact, the behavior with respect to deformation is that of a weak elastic solid which is broken by passage through a capillary tube. The light-scattering capacity remains surprisingly low. Any agency such as pH, temperature, salts, or gelatin concentration, which prevents the formation of a gel likewise prevents the characteristic increase in optical activity.²

This simultaneous appearance of gel formation, high specific rotation, and low Tyndall effect just adjacent to a region of precipitation is significant. The incipient or unsuccessful precipitation which may be considered as the origin of gel formation does not appreciably modify the *optical heterogeneity* with respect to the visible portion of the spectrum (as shown by the Tyndall effect), but does greatly modify the *optical rotatory power*. The rigidity and elasticity characteristic of the gel state may arise without the appearance of the grosser features associated with advanced stages of precipitation. It may be supposed that when the tendencies to precipitation and solution (or peptization) are so nicely balanced as they appear to be in a gel, the intermicellar bonds (of whatever type they may be) give rise to a state of intramicellar or intramolecular strain which modifies the rotatory power in a way that can not be described in simple terms of asymmetric carbon atoms. Since the specific rotation of gelatin changes so slightly with change in pH (if gel formation is prevented by salts or proper temperature), the stresses resulting from the cohesion of the gel structural elements may be considered as being more uniformly distributed throughout the micells or molecules and therefore more effective in determining optical activity than the localized stresses accompanying combination with acid or base. To the extent that the rotatory power may vary in a *continuous* manner³ with varying conditions, the optical activity of gelatin gels may be analogous to that which normally inactive bodies display when strained by external stresses.

¹ Kraemer and Dexter: *J. Phys. Chem.*, 31, 764 (1927); Joseph: Ph. D. Thesis, Univ. of Wisconsin (1927).

² Further examples of this parallelism are given in a recent paper by Carpenter: *J. Phys. Chem.*, 31, 1873 (1927).

³ Changes in chemical structure, being molecular, necessarily cause discontinuous changes in rotatory power.

Although it has not been customary to recognize any direct dependence of optical activity upon colloidal processes, a search of the literature reveals isolated observations apparently analogous to the gelatin systems in this respect. Striking examples occur with cellulose triacetate in pyridine,¹ derivatives of cellulose and lichenin,² and particularly with the potassium salts of α , β stearin sulfuric and phosphoric acids.³ Certain soluble starch⁴ and cellulose systems⁵ are possibly also examples. It is quite likely that other cases of this kind would be found upon investigation. The phenomenon is therefore a general one, and may well provide a means of studying colloidal processes in a variety of systems.

The very generality of the dependence of rotatory power upon colloidal features detracts from the attractiveness of current hypotheses involving tautomeric changes between "sol form" and "gel form" as an explanation of "mutarotation" and gel formation in gelatin systems. The immediate cause of the rotatory behavior in all probability resides in structural features characteristic of the gel state and supermolecular in scale.

The detailed results of this paper deal only with the optical activity of dilute aqueous gelatin systems and its dependence upon temperature, pH, specific electrolyte, and gelatin concentration. Gel formation and resistance to shear will be treated specifically in a later communication.

Procedure

Unless specifically stated to the contrary, the gelatin used in this work was a de-ashed hide gelatin procured from the Eastman Kodak Company and electro-dialyzed to the isoelectric point in this laboratory. The ash content, on the basis of vacuum dried gelatin, was 0.05 percent.

In order to insure uniformity in the series of gelatin systems to be used in the study of a given factor, a common stock was prepared in sufficient quantity to serve as the source of the series of samples. Portions of this stock were diluted by weight with standard acid or alkali and redistilled water to the desired gelatin concentration and pH, and heated to 50°C for twenty minutes to destroy the influence of previous thermal history. Portions of these systems were then placed in thermostats at the desired temperatures and allowed to attain approximate "optical equilibrium." The rotations of these systems were determined for the 546.1 m μ line of mercury isolated from the radiations of a mercury vapor arc by means of the Wratten filter 77A. Specific rotations were calculated in the usual way:
$$\left[\alpha \right]_{546.1}^{t^{\circ}} = \frac{100\alpha}{g d l}$$
 The temperatures of the polarimeter tubes during the measurements were controlled to 0.1° between 15° and 40°C, to 0.2° at 10° and 50°C, and to 0.5° for temperatures at 5°C or below.

¹ Hess: *Z. angew. Chem.*, 37, 997 (1924); Hess and Schultze: *Ann.*, 455, 101 (1927).

² Pringsheim, Leibowitz, Schreiber, and Kasten: *Ann.*, 448, 177 (1926); Bergmann and Knehe: *Ann.* 452, 151 (1927).

³ Grün and Limpächer: *Ber.*, 60, 255, 266 (1927).

⁴ Pictet: *Helv. Chim. Acta*, 9, 33 (1926).

⁵ Atsuki et al: *J. Cellulose Ind. Tokyo*, 1, 53 (1925); 2, 3 (1926).

The pH values of the systems were determined at room temperature with the hydrogen electrode combined through a 1.N potassium chloride bridge with the normal calomel half cell, the potential of which was assumed to be + 0.2848 volts at 25°C, referred to the normal hydrogen electrode. No correction was applied for the boundary potential.

The reproducibility of the observations varied with the conditions. Duplicate samples prepared from a common stock and run simultaneously usually checked in their rotations to 1 percent or better. When such samples were not run together, discrepancies might amount to 2 or 3 percent. Gelatins from different sources, even though they were of the same type, revealed much greater differences in rotatory power. Specific cases of large experimental error will be pointed out in the appropriate places.

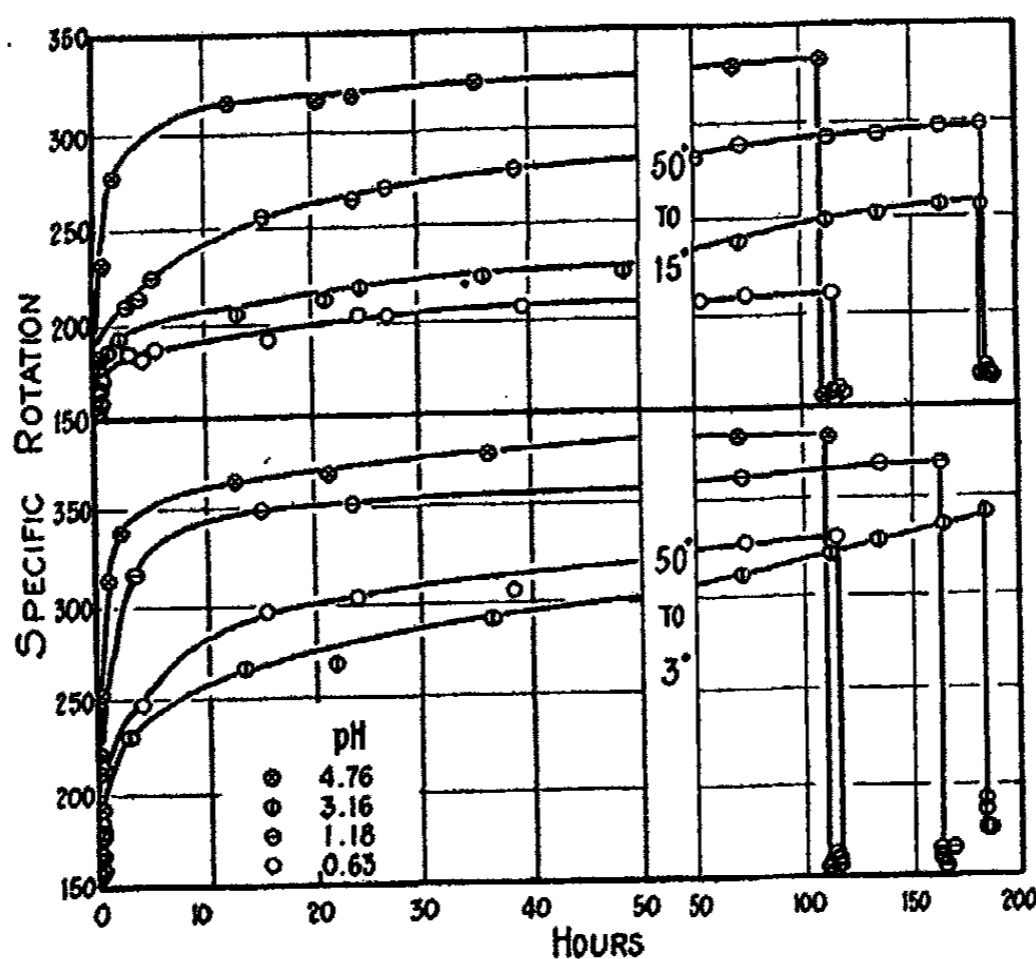


FIG. 1

Rate of change in specific rotation of 0.52% gelatin systems following a sudden drop in temperature from 50° to 15°C (upper group of curves) or to 3°C (lower curves). pH values adjusted with hydrochloric acid. The final drop in rotation occurred upon restoring the temperature to 50°C.

Kinetics of Change in Rotatory Power

At temperatures which did not permit the formation of gels (as above 30°C) the change in optical activity following a change in temperature took place very rapidly; optical equilibrium and thermal equilibrium were attained almost simultaneously. Under other conditions the rate of change in rotatory power was easily susceptible to measurement. A detailed study of the kinetics is well worthy of study. This aspect, however, was considered only in so far as was necessary to determine the time required for the attainment of steady rotation under chosen conditions.

The rotation at 50°C was selected as a starting point for observations of changing rotatory power. At this temperature no influence of previous thermal history at lower temperatures was evident. Within thirty minutes the rotations were essentially constant, unless the pH was sufficiently high or low to cause noticeable hydrolysis or racemization. Samples were quickly cooled from 50°C to either 15° or 3°C, and the rotations were observed at frequent intervals at these temperatures. At the end of the experiments the specimens were warmed to 50°C to determine whether any irreversible change had taken place during the low temperature period. The results of typical experiments are presented in Figures 1 and 2.

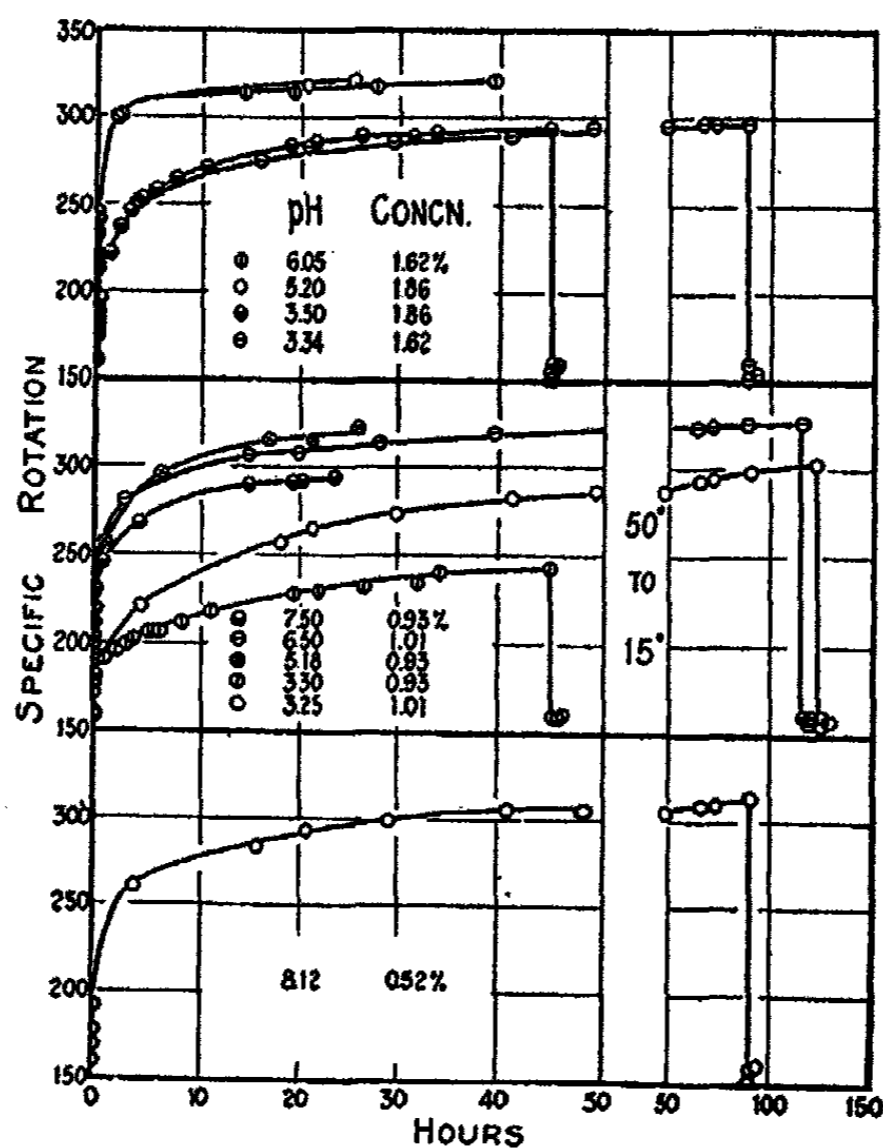


FIG. 2

Rate of change in specific rotation of gelatin systems of different concentrations and pH following a sudden drop in temperature from 50° to 15°C. pH values were adjusted with acetic acid or sodium hydroxide. The final drop in rotation demonstrates the reversibility upon restoring the 50°C condition.

It is immediately evident that the time required for the attainment of a constant rotation may vary considerably. In general, however, the rapidity with which a large fraction of the total change in rotation takes place increases with the magnitude of the total change. Because of the protracted character of the change—especially in the systems showing a slighter tendency to gel formation—it is in some cases impossible to specify a well defined equilibrium value for rotatory power. The curves for rotations at 3°C even suggest that a common equilibrium value is being approached. Gelatin systems are too la-

bile, both chemically and physically, to justify an indefinite extension of the observations. For comparative purposes, the rotations at the end of 72 to 75 hours at 3° and 15°C were selected as "equilibrium values." Correspondingly shorter periods were chosen to give the "equilibrium values" at higher temperatures: 20° to 25°C—24 to 36 hours; 30° to 40°C—8 to 10 hours; 50°C—30 to 60 minutes.

The quantitative formulation of the course of the changing rotation should throw light on the character of the process. It has not yet been possible, however, to give a rational quantitative interpretation to the data. It is

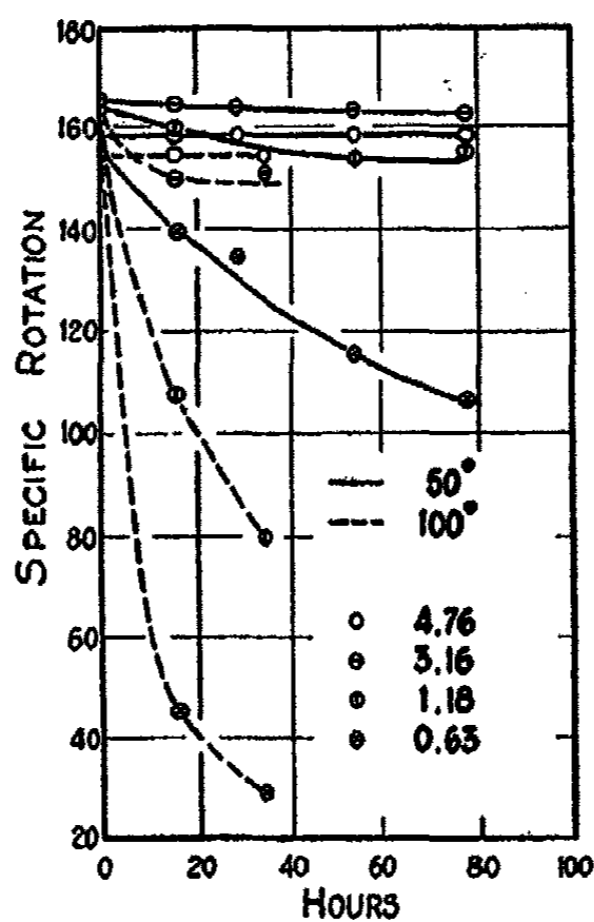


FIG. 3

Effect of hydrolysis upon the specific rotation of 0.52% gelatin systems at different pH values.

evident from casual observation of the curves that the laws for simple bimolecular reactions are not consistent with the optical behavior recorded.¹

Neither does Wo. Ostwald's empirical method² of expressing Trunkel's³ results by means of parabolic equations have any general applicability. The curves for log (change of rotation) vs. log time were found in this work to be convex to the time axis.

The reversibility of the rotation changes is of particular interest in connection with the interpretation of the phenomena. In practically all cases—even at rather extreme pH values—the increase in temperature from 3° or 15°

¹ Cf. however C. R. Smith: *J. Am. Chem. Soc.*, 41, 135 (1919), who found these laws to apply to limited portions of the change. In their preliminary paper, the present authors have raised various objections to this interpretation of the sol-gel change as a bimolecular reaction.

² Wo. Ostwald: *Kolloid-Z.*, 17, 113 (1915). See also de Izaguirre: *ibid.*, 33, 337 (1923).

³ Trunkel: *Biochem. Z.*, 26, 493 (1910).

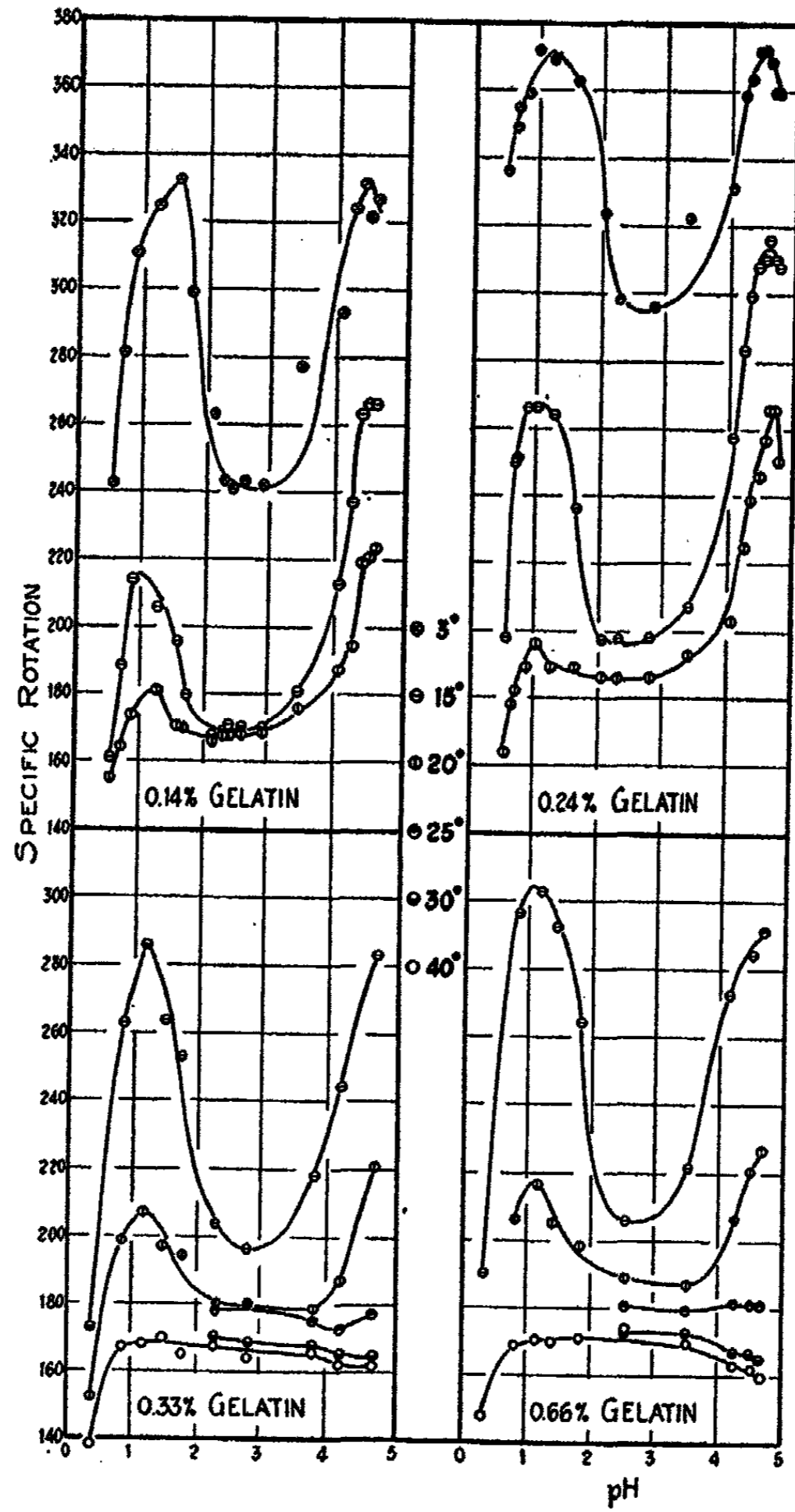


FIG. 4
Influence of pH, specific electrolyte, and temperature upon the specific rotation of 0.38% gelatin systems.

to 50°C restored the original rotations within the limits of experimental error. The effects of hydrolysis or racemization were therefore presumably absent. The changes in rotatory power are directly associated with the reversible changes responsible for the sol-gel transformation.

At higher temperatures, however, irreversible changes in rotation do take place as a result of hydrolysis. To illustrate, samples from the stocks which yielded the curves in Fig. 1 were heated in sealed tubes at 50° and 100°C. After various intervals portions were removed and their rotations determined at 50°C. The results appear in Fig. 3.

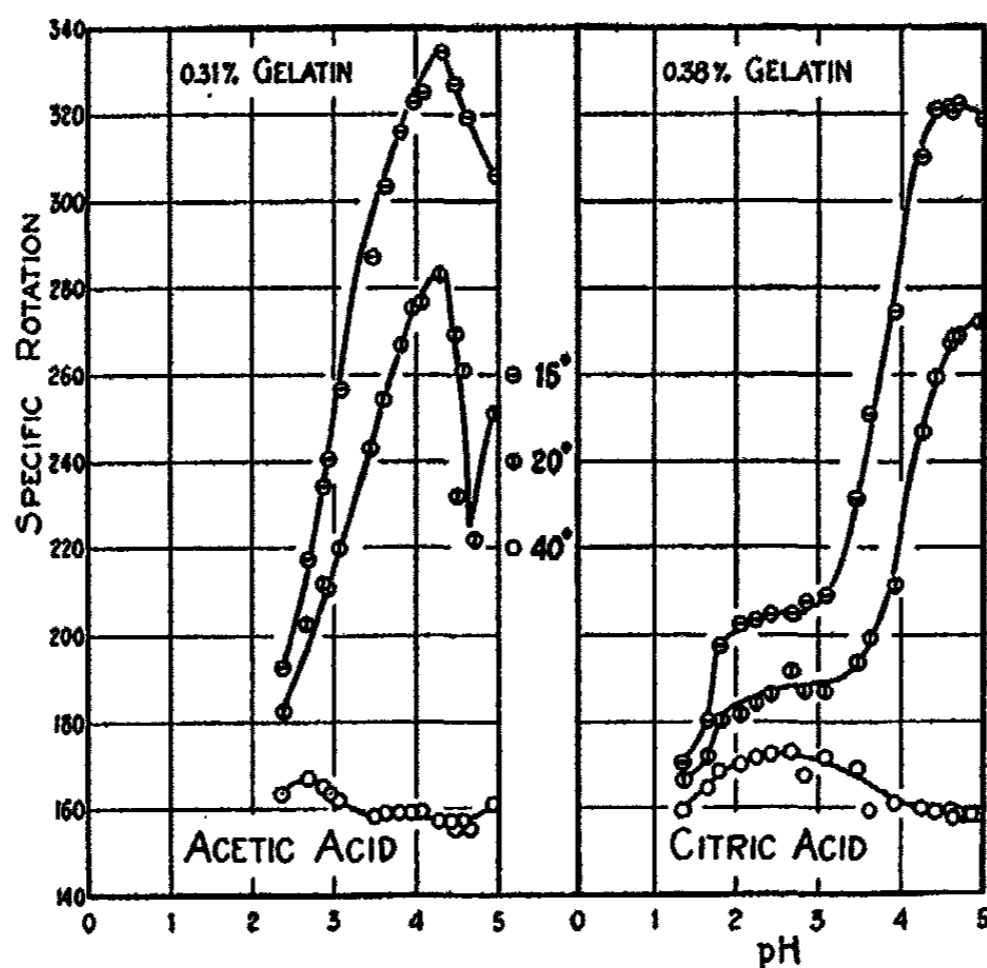


FIG 5
Influence of pH, specific electrolyte, and temperature upon the specific rotation of gelatin systems.

At 50°C the influence of hydrolysis upon rotation is small except at such extreme pH values as 0.63. At 100°C the rotations fall rapidly unless the samples are at or near the isoelectric point condition. The rates of these irreversible changes depend upon pH and temperature; but the optical behavior to which attention is particularly directed in this paper (at 50°C and below) is independent of these irreversible changes in the gelatin.

Influence of Acids, Bases, and Gelatin Concentration upon Specific Rotation of Gelatin Systems at Various Temperatures and pH Values

In the earlier paper results were presented which show the influence of pH and temperature upon the "equilibrium" optical rotations of 0.47% aqueous gelatin systems containing acetic acid or sodium hydroxide. As the most striking feature, attention was directed to the two types of pH-specific rotation curves obtained. Above 27.5°C the isotherms resemble the corre-

sponding curves for such properties as have been partially described in terms of the Procter-Wilson theory of gelatin behavior. They exhibit a minimum rotation at the isoelectric point (pH 4.9), another poorly defined minimum between pH 8 and 9, and a decrease in rotation at the extreme pH values.

Below 25°C the specific rotation-pH curves are of quite a different type. In the isoelectric regions the specific rotation rises to a maximum where, at higher temperatures, a minimum appears. At adjacent pH values minima appear where maxima appear at higher temperatures. The regions of high specific rotation at the lower temperatures correspond to the regions of most pronounced gel formation. The change in the type of the specific rotation-pH curves between 25° and 27.5°C corresponds to the sol-gel transformation.

The studies have been repeated and extended to include different gelatin concentrations and a variety of acids and bases for controlling the pH. In Figs. 4-10 inclusive are presented the results in the form of "equilibrium" specific rotation-pH curves.

Effect of Acids:—

In Figs. 4 and 5 it may be seen that other acids than acetic acid also give two types of curves, one characteristic of temperatures of 40°C or above, one characteristic of temperatures of 25°C or below. Although the temperature intervals were too wide to make an accurate estimate possible, it seems probable that the temperature of transition between the types of curves is approximately uniform for all the acids used.

The 40°C curves present no new features. The specific rotations for any given acid do not vary greatly with change in pH. With the exception of the hydrobromic acid curves the absolute magnitudes of the rotations appear essentially independent of the acid radical present. At a pH of 2.5-3.0 the specific rotation is 170°. In the presence of hydrobromic acid the rotation is but 160°. It is uncertain to what cause this difference may be assigned.

The low temperature curves are essentially uniform at pH values greater than 2.0 which was the lower limit reached with acetic acid in the preliminary report. The specific rotation rises very rapidly as the isoelectric point is approached and gel formation sets in. The lower the temperature the more pronounced is gel formation and the greater is the specific rotation. If gelatin systems at pH values below 5 be considered as containing a mixture of isoelectric gelatin and gelatin combined in some way with acid or hydrogen ions, the specific rotation curves indicate that a decrease in temperature below 40°C causes a much greater change (in terms of the magnitude of the rotation) in the isoelectric gelatin than in the acid-gelatin complex. In a general way, the fall of specific rotation as the pH changes from the isoelectric point to pH 2.0 suggests a direct and simple relation between extent of acid combination and rotatory power over this region. A quantitative correlation, however, is not easily carried through because of the complicated relationship between specific rotation and gelatin concentration.

Just at the isoelectric region, within which the precipitation tendency is so marked as to give gross turbidities,¹ the new data usually reveal a minimum specific rotation (Cf. Fig. 10, covering both sides of the isoelectric point). Because of the narrow range and the interfering turbidity this minimum was overlooked in the earlier work by the authors as well as by Vlès and Vellinger. This narrow and erratic minimum in all probability does not indicate any new

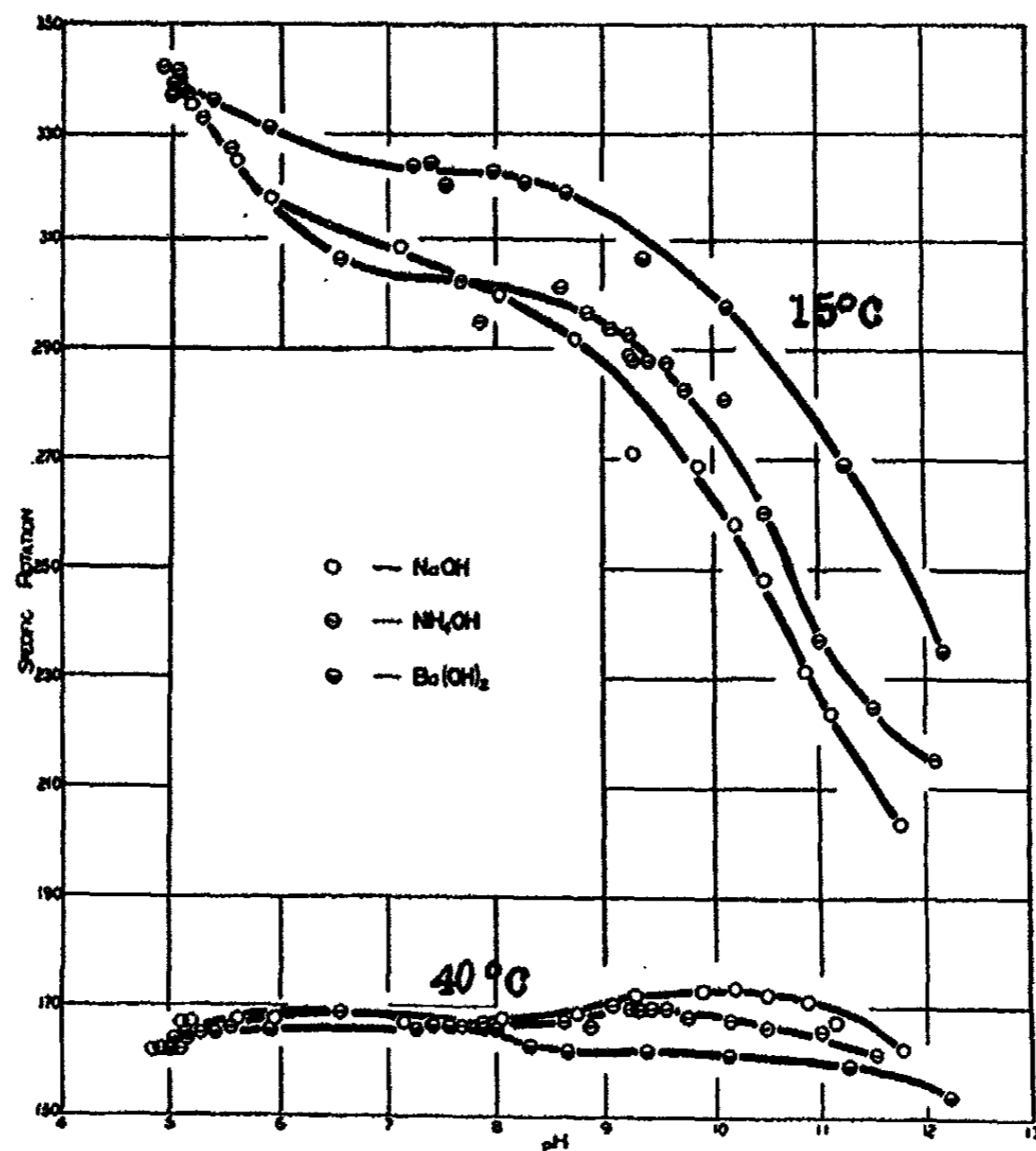


FIG. 6
Influence of pH, specific electrolyte, and temperature upon the specific rotation of 0.41% gelatin systems.

change in the highly dispersed gelatin, but likely arises because the precipitation causing the turbidity removes gelatin from the optically active dispersed state.

The new and surprising features brought out by the later work occur at pH values below those attainable with acetic acid. In the neighborhood of pH 1 another maximum in rotation appears at temperatures below 25°C. At 40°C or above a more or less distinct minimum specific rotation takes the place of the maximum. This transition of a minimum rotation to a maximum rotation at low pH values as the temperature falls closely resembles the cor-

¹ Kraemer and Dexter: J. Phys. Chem., 31, 764 (1927).

responding transition associated with the sol-gel change taking place near the isoelectric point. In both cases the maximum specific rotation is accompanied by a maximum in the tendency for gel formation. In both cases the gel formation is closely associated with and just adjacent in pH to regions of low degree of dispersion or actual precipitation.¹

An apparent exception to this behavior is presented when the pH values are adjusted with citric acid, Figure 5. Below a pH of 2 the specific rotation falls sharply instead of rising. The parallelism between specific rotation, gel formation, and coarseness of dispersion is maintained, nevertheless. At low pH values with citric acid no gel forms in the concentrations used, and no increase in Tyndall intensity occurs as the temperature falls below 25°C. The anomaly is undoubtedly due to peptization effects arising in concentrated solutions, for at pH 1 the solution is almost saturated with citric acid.

With the exception of the citric acid series, no striking specific behavior occurs with the acids used. The greater breadth of the low pH maximum and the increased values of the specific rotation when sulfuric acid is used are real, but minor differences. In analogous fashion, the tendency to gel formation is greater in the presence of sulfuric acid than in the other acids. With respect to specific rotation and gel formation, the use of sulfuric acid is equivalent to a decrease in temperature with the other acids. This effect is to be classed as a lyotropic one.

Effect of Alkalies:—

The combined influence of temperature, pH, and specific electrolyte upon the specific rotation of gelatin systems on the alkaline side of the isoelectric point was also studied. The pH values were adjusted with sodium, ammonium, or barium hydroxides. The gelatin concentration was 0.41%. The data are given in Fig. 6.

Between pH 4.9 and 8.0 at 40°C the specific rotation is almost uniform for the three alkalies. Beyond pH 8 an appreciable divergence of the three curves takes place. The influence of the specific alkali is least evident near pH 5 and 8.

At 15°C the specific rotation rises in all three cases to a major maximum near the isoelectric point and a secondary maximum, partially masked by its adjacency to the major maximum, near a pH of 8. At all pH values barium hydroxide gives greater specific rotations at 15°C and a greater tendency to gel formation than do the other alkalies. Gel formation and high specific rotation go hand in hand above as well as below pH 5.

The reversal in the order of the curves at 15°C and 40°C above pH 8 is curious and not explicable at present. On the whole, the curves do not reveal any simple valence effects.

Effect of Gelatin Concentration:—

Two groups of experiments were performed, one in which the pH values were adjusted with hydrochloric acid, the other in which acetic acid or

¹ A maximum in Tyndall intensity—pH curves at low temperatures appears near pH 1. G. H. Joseph, Ph.D. Thesis, Univ. of Wisconsin, 1927.

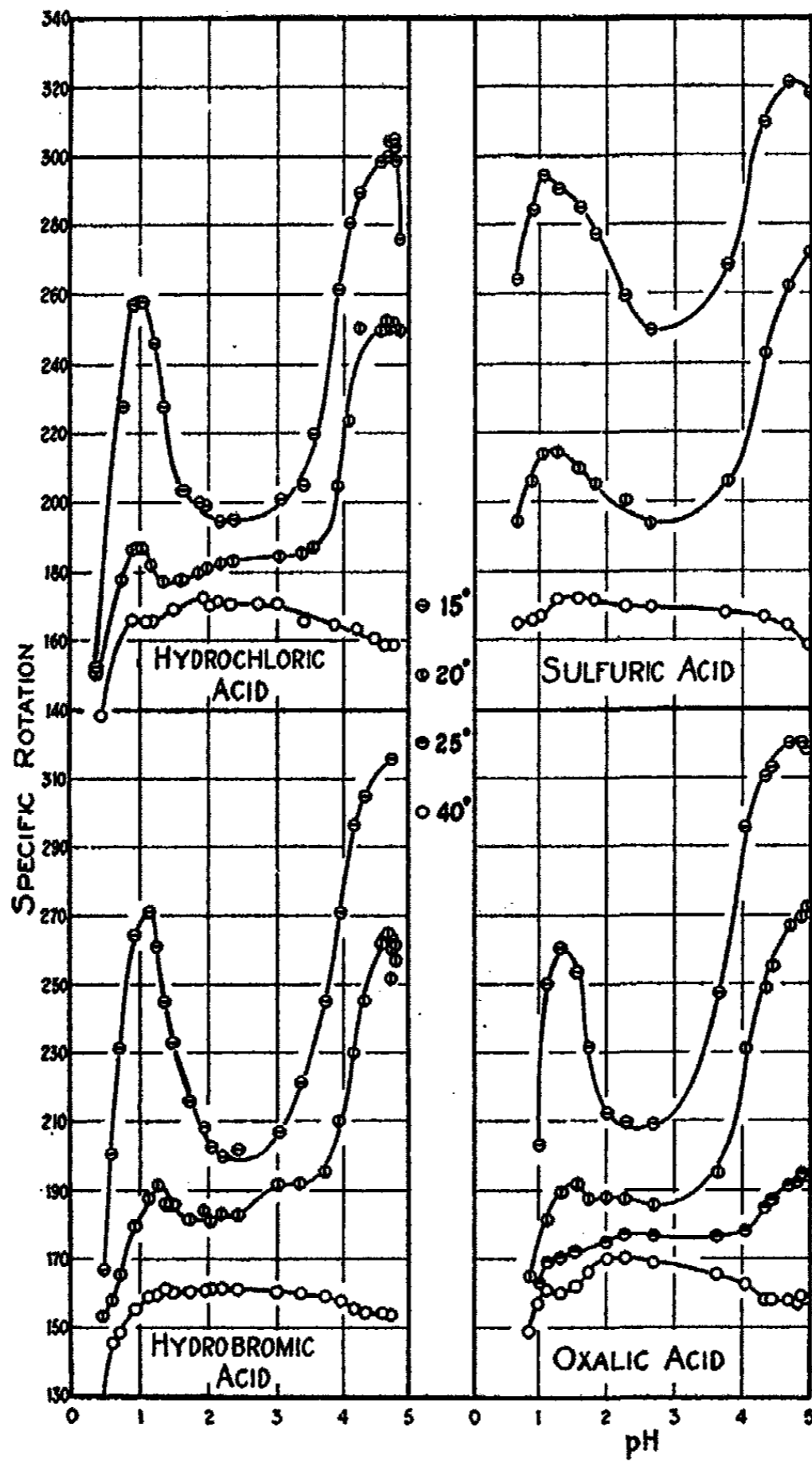


FIG. 7

Influence of gelatin concentration upon specific rotation at various temperatures. pH's adjusted with hydrochloric acid.

sodium hydroxide was used. The data for the first group are presented in Figs. 7, 8, and 9, which cover concentrations from 0.14 to 2.80% inclusive. Curves for the second group dealing with concentrations from 0.31 to 1.24% appear in Fig. 10.

With the exception of some minor irregularities, due to rather large experimental error or the necessity of using different batches of gelatin, the specific rotations appear to be independent (within a few percent) of gelatin

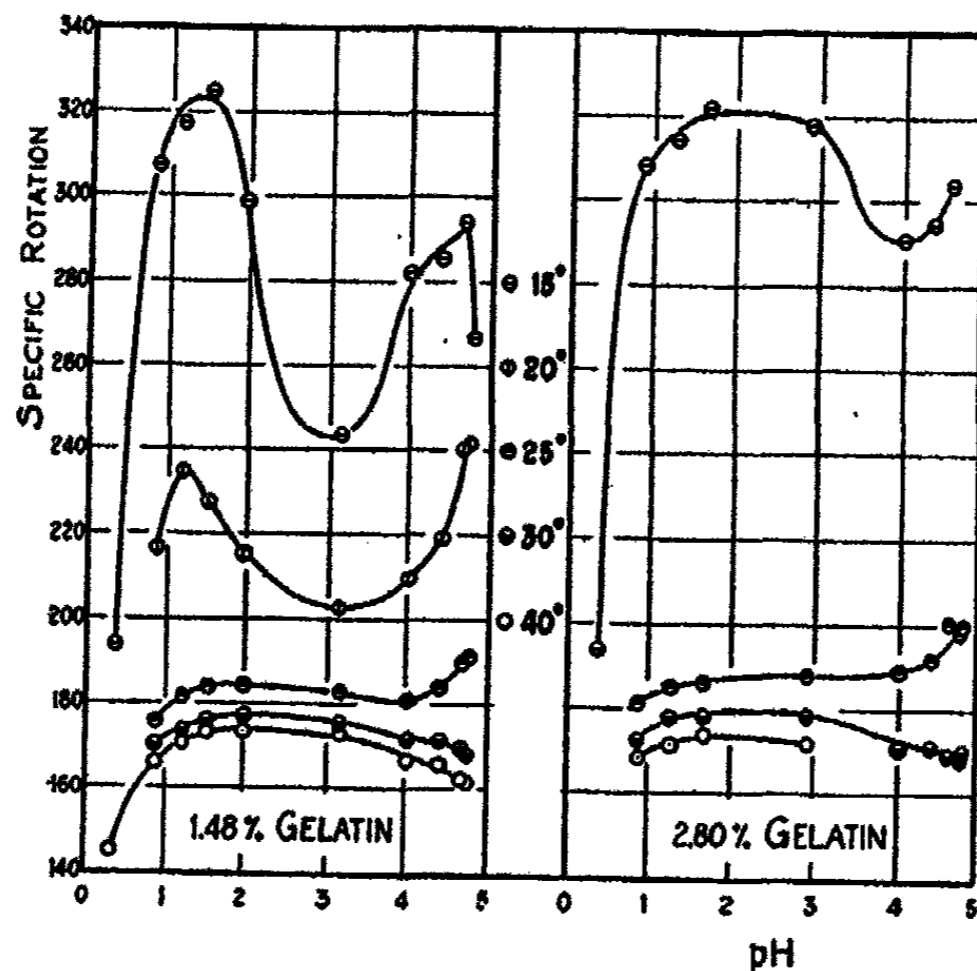


FIG. 8

Influence of gelatin concentration upon specific rotation at various temperatures. pH values adjusted with hydrochloric acid.

concentration at temperatures of 30° or above. This independence of course probably does not persist into high concentrations.

Within the concentration range studied, the transition in type of rotation-pH curve remains between 25° and 30°C.

Figs. 7, 8, and 9 show that at lower temperatures the specific rotation increases with the concentration, with the more pronounced increase taking place in the valley between the two maxima (pH 2-4). The irregularities apparent in Fig. 9 are due to the fact that different batches were used for the two lowest and the four highest concentrations. The behavior of each batch was, however, consistent with the rule just stated. It is probable that at somewhat higher concentrations than those used the specific rotations attain a maximum value which may be almost constant between pH values 1 and 5.

The tendency to gel formation increases with the concentration in the same relative way as the specific rotation. A higher concentration or a lower

temperature is necessary to attain a given specific rotation or gel formation at pH 3 than is needed at pH 1 or 4.5.

Although the curves of Fig. 10 present some irregularities—as the order of the curves for 20°C at pH values below 5, or the position of the 0.62% curve in the alkaline region—they agree with Figures 7, 8, and 9 in most points. At 40°C the specific rotation does not vary greatly with concentration. At

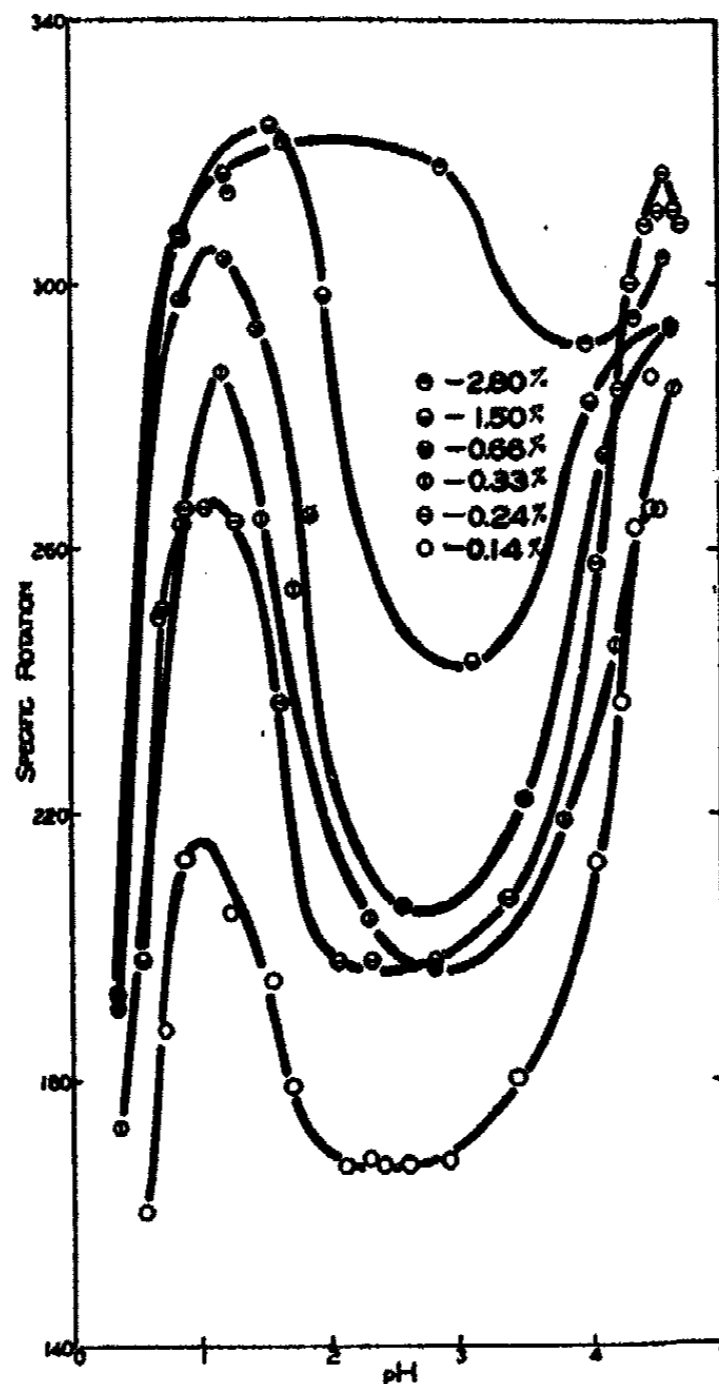


FIG. 9

Influence of gelatin concentration and pH upon the specific rotation of gelatin systems at equilibrium at 15°C. These curves summarize the data for 15°C in Figs. 7 and 8.

20° and 15°C the increase in specific rotation with concentration is greater in the valleys than on the maxima. Just as on the acid side, the specific rotation at low temperatures or high concentrations tends to reach a maximum value independent of pH between 5 and 10. These curves illustrate plainly the minimum in specific rotation caused by partial precipitation at the isoelectric point.

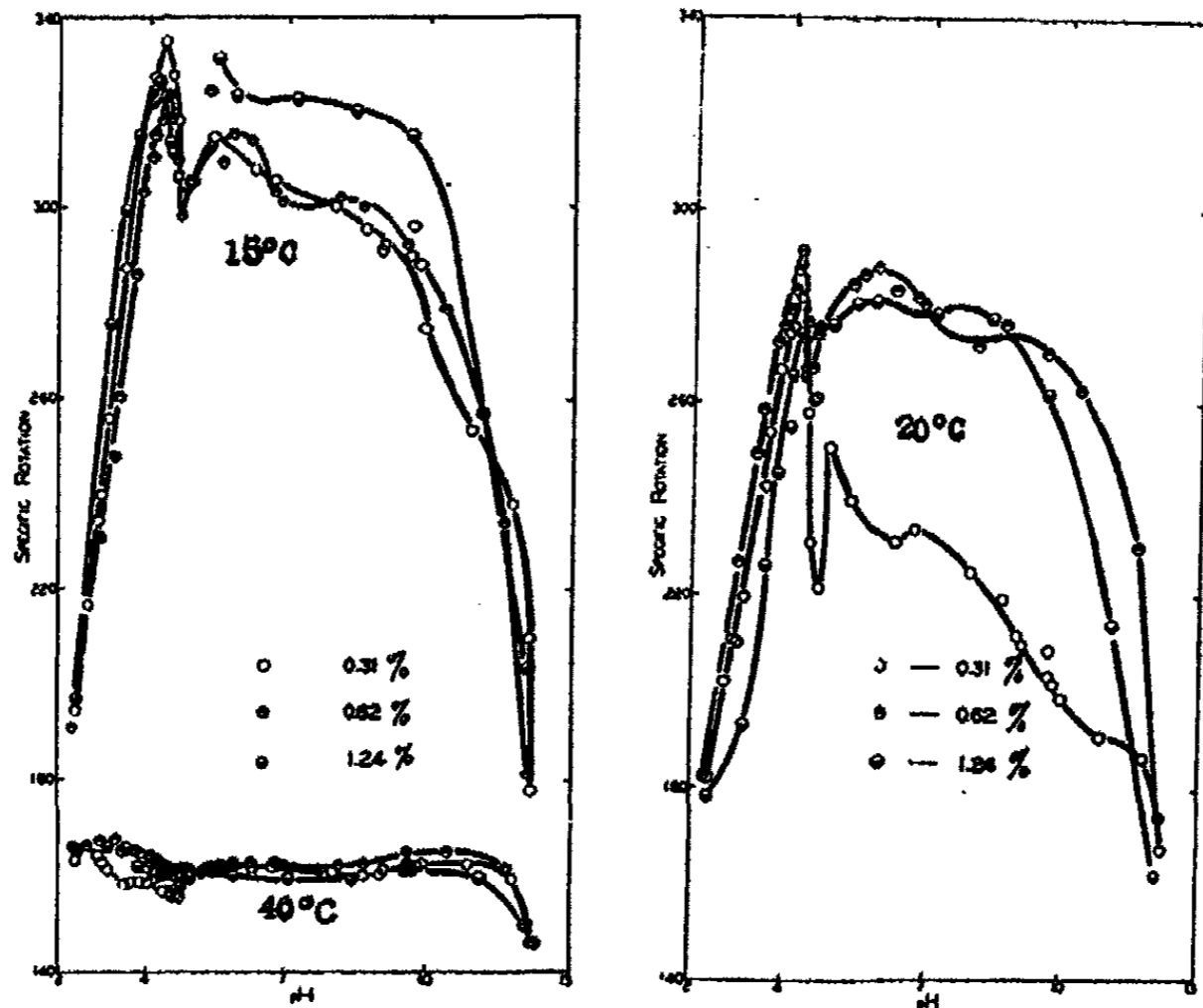


FIG. 10

Influence of gelatin concentration, temperature, and pH upon the specific rotation of gelatin systems. pH's adjusted with acetic acid or sodium hydroxide.

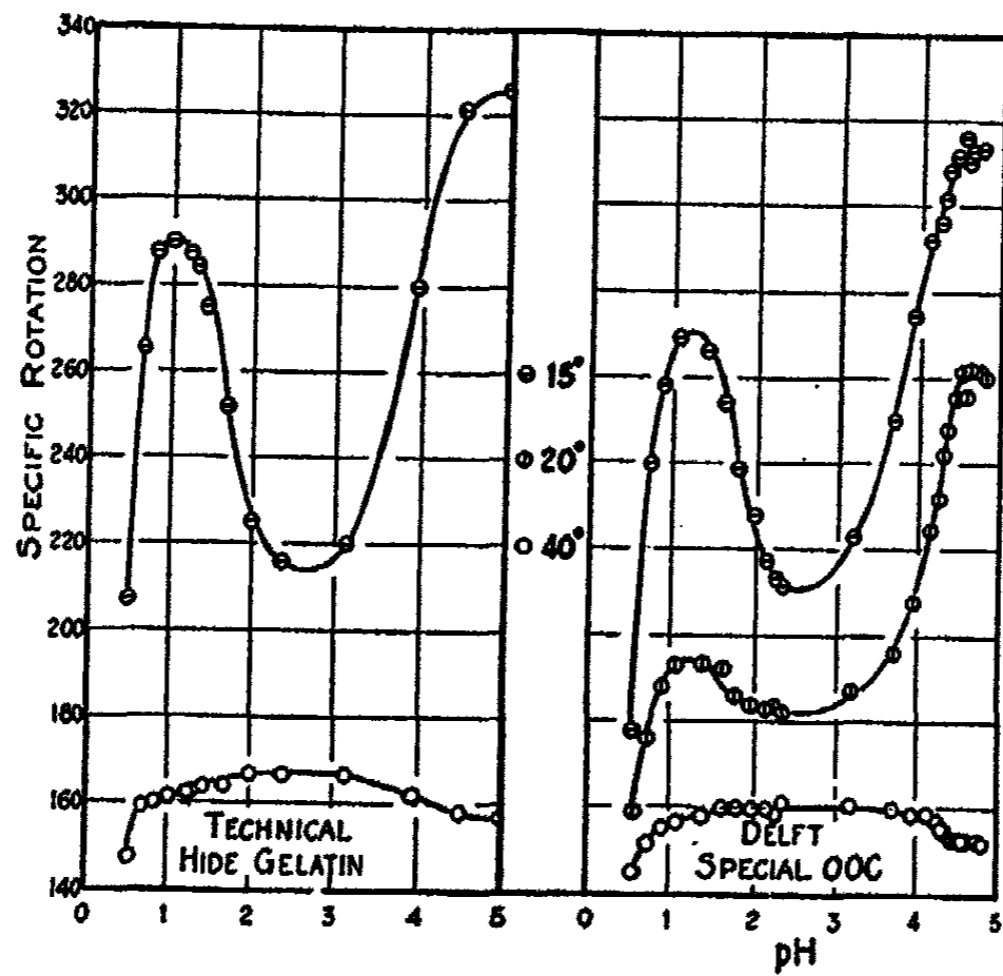


FIG. 11

Optical behavior of gelatin from different sources. Concentration—0.41%. pH's adjusted with hydrochloric acid.

On the alkaline side the double maxima in the curves are not fictitious, although their location or absolute height may be subject to a larger experimental error because of ill defined pH values in the absence of buffers. The less pronounced maximum corresponds to the discontinuities shown in other properties in the neighborhood of pH 8.

Rotatory Power of Gelatins of Different Types

An extension of the investigation to other gelatin types showed that the behavior described above is not peculiar to one particular type of gelatin.

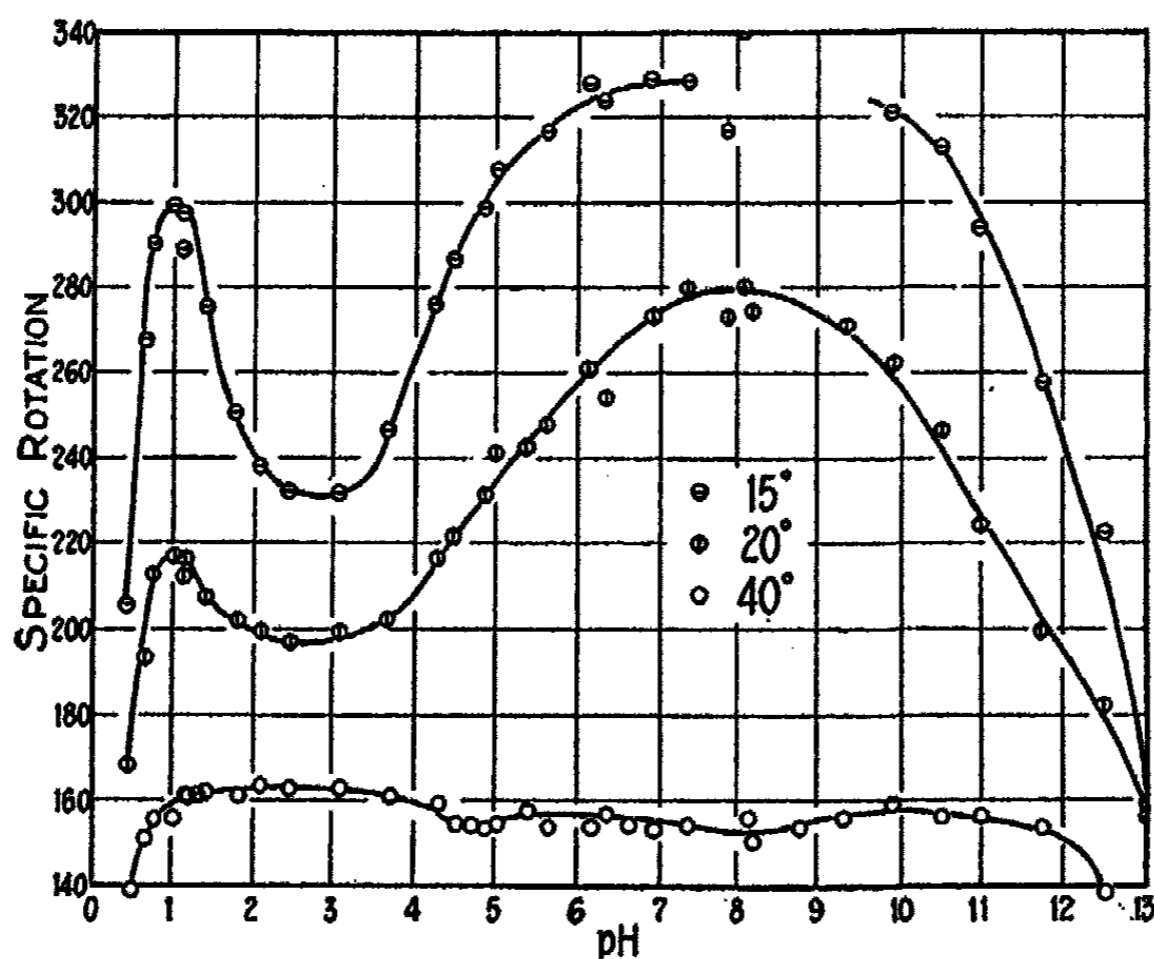


FIG. 12

Optical activity of Gray's Lake "Superior Quality" pig skin gelatin with hydrochloric acid or sodium hydroxide. Concentration—0.4%.

In Fig. 11 are given results obtained with the hide gelatin from which the de-ashed product used in the body of this work was prepared. The curves duplicate within the limits of experimental error the corresponding ones given for the de-ashed material.

Curves are also given in Fig. 11 for a commercial blended bone gelatin. The behavior of this product closely resembles that of the hide gelatin. The two 40°C curves in Fig. 11, like those of earlier figures, show a constant specific rotation adjacent to the isoelectric point, which is not easily correlated with the acid combination curve.

A highly anomalous behavior was found in the case of a pig skin gelatin (Fig. 12). At 40°C the specific rotation is normal with respect to absolute values as well as number and location of maxima and minima. At lower temperatures, a transition in type of curve appears which parallels gel forma-

tion in a normal fashion. The usual maximum in specific rotation and gel formation appears at pH 1, but at higher pH values the low temperature curve differs markedly from those of the other gelatins. There is no discontinuity at pH 5, notwithstanding the normal appearing minimum at higher temperatures. The dominant maximum which would ordinarily be used to locate the isoelectric point appears at pH 8 and is exceptionally broad. It has been previously shown that there is a broad maximum in light scattering capacity (i.e. precipitation tendency) under these same conditions.¹

These striking differences in the pH effects distinguish the pig skin product from the ordinary gelatins and characterize it as a different protein. Notwithstanding this it displays the same relationships between precipitation tendency (or Tyndall intensity), gel formation, and optical activity as are to be found in the ordinary gelatins. As was pointed out in the introduction, the close association between optical activity and gel formation is a general phenomenon rather than a special peculiarity of a single material.

Summary

The influence of pH, temperature, specific electrolyte, and gelatin concentration upon "equilibrium values" for the optical rotation of dilute aqueous dispersions of de-ashed gelatin has been studied.

At temperatures above 30°C the specific rotation is approximately independent of pH, temperature, specific electrolyte, or gelatin concentration between rather wide limits for these variables. *Minimum* rotations more or less clearly defined may appear at pH values near 1, 5, and 8.5 with rapid falls in rotation at the two extremes.

At temperatures below 25° *maximum* rotations appear near pH values 1, 5, and 8.5. With low gelatin concentrations and low temperatures, the maxima and minima are very pronounced; at higher concentrations they tend to disappear. The specific influence of different electrolytes is noticeable, but not striking in moderate concentrations. Such as they are, they resemble lyotropic rather than valence influences. At these temperatures the rotatory power adjusts itself with measurable speed to change in temperature (so-called mutarotation).

A comparison of the optical behavior with the colloidal behavior (particularly the capacity to form gels) reveals a surprisingly detailed parallelism between these two aspects. Gel formation in dilute systems is invariably accompanied by a pronounced mutarotation and a high specific rotation. Any agency which prevents the appearance of a high specific rotation prevents gel formation.

The appearance of this dependence of rotatory power upon gel formation in systems other than normal gelatin suggests that the phenomenon is not peculiar to gelatins, but is general to optically active systems capable of

¹ Kraemer and Dexter: *J. Phys. Chem.*, 31, 764 (1927).

forming gels. This supposition is supported by a number of isolated observations to be found in the literature.

The anomalous rotatory behavior associated with gel formation probably does not reflect intramolecular changes of the sort that can be given simple stereochemical interpretation with the help of asymmetric carbon atoms. It is more likely that the intermicellar cohesion accompanying the incipient precipitation responsible for gel formation indirectly modifies the intramolecular structure by exercising what might be called a distributed stress. In the special case of gelatin, this "distributed stress" is much more effective in controlling rotatory power than the more localized stresses associated with acid or base combination.

DEVELOPMENT OF A METHOD OF RADIATION CALORIMETRY,
AND THE HEAT OF FUSION OR OF TRANSITION OF
CERTAIN SUBSTANCES*

BY LUKE E. STEINER** AND JOHN JOHNSTON

It is, for many reasons, advantageous to have more extensive and more reliable data on the heat of fusion of related organic compounds than are now available. To make such determinations by the usual method, which consists essentially in dropping the substance, successively heated at a series of temperatures about its melting point, into the calorimeter, is somewhat tedious, and it is necessary to secure a considerably better degree of accuracy in the individual observations than is desired in the heat of melting. Moreover, this method is not feasible unless the melted substance, when rapidly chilled on entering the calorimeter, crystallizes completely in its stable form.

The method to be described is that which has been called radiation calorimetry; a comparison method in which known heats are used in standardizing an apparatus for the determination of unknown heats, and as such is comparable to the rapid methods of volumetric analysis in analytical chemistry. In essence it utilizes the rate of heat loss (or gain) of a body, under a difference in temperature between the body and its surroundings, as a measure of the change of heat content of the body. A relation between the rate of temperature change of a body and the effective thermal head,¹ was first formulated by Newton²; this relation, called Newton's law of cooling, is shown to be a special case of a more general relation, connecting change of heat content with thermal head, which is valid in the apparatus as developed.

The method of radiation calorimetry has application not only to evaluation of heats of fusion, but in general to any chemical reaction which proceeds at a definite temperature maintained throughout the reaction by the evolution or absorption of heat. It can therefore be applied to determine the heat of transition of a polymorphous solid, if the condition stated above is fulfilled. It has special advantages in the determination of the heat of reaction of certain irreversible processes, such as the heat of fusion of unstable crystalline forms. It also lends itself to technical application for the method can be made automatic by the suitable use of recording and regulating instruments.

* Contribution from the Department of Chemistry, Yale University.

** Holder of a Sterling Junior Fellowship, 1926-27. From a thesis submitted in June, 1927, to the Graduate Faculty of Yale University in candidacy for the degree of Doctor of Philosophy.

¹ The thermal head, analogous to the head in hydrostatics, is defined as the temperature difference which determines the direction and magnitude of heat flow, i.e., the effective temperature difference between a body and its surroundings.

² *Scala Gradum Caloris*, Phil. Trans., 22, 824 (1701).

The Time-Temperature Curve

Since the time-temperature curve is used in all determinations of heat by radiation calorimetry its interpretation must be considered. In general both heating and cooling curves may be discussed in an analogous manner; so that it will be necessary to consider only one in detail. The cooling curve was chosen for this purpose, for it has a peculiarity due to the undercooling of a liquid when there are no crystals present at the freezing temperature, there being usually no analogous super-heating of a melting solid. It should be

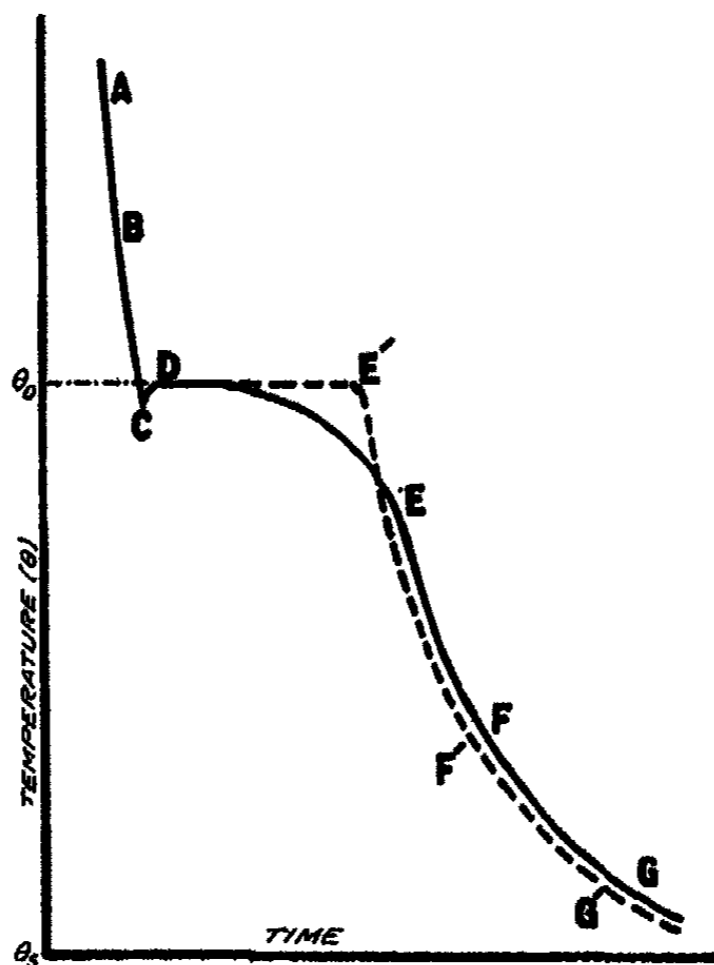


FIG. 1

Typical experimental and limiting cooling curves for a substance undergoing change of state under unregulated cooling.

understood, however, that precisely the same deductions may be drawn from the heating curve and that the formulæ which are derived apply to it as well as to the cooling curve.

Time-temperature curves may be classed as regulated or unregulated curves, depending on the effort made to control the rate at which heat is exchanged between the cooling (or heating) body and its surroundings. In order to ascertain the precise experimental precautions which must be observed if reliable results are to be secured, it may be well to analyze an unregulated curve (as in Fig. 1) of the type recorded by previous workers along these lines. The curve ABC represents the cooling of the liquid, CDE' the freezing of the liquid, and E'F'G' the cooling of the solid. At A the rate of cooling is rapid; it falls off as the temperature (θ) of the body approaches that of the surroundings (θ_s) and becomes small as the thermal head ($\theta - \theta_s$) becomes small. If the thermal head is large, as is usually the case with unregulated

cooling, the temperature of the freezing substance may follow the curve CDEFG since rapid cooling may preclude uniformity of temperature throughout the specimen. Unregulated cooling curves tend to follow the continuous curve (Fig. 1) and only approach the "ideal" broken curve as a limit. To prevent such changes in the rate of cooling as are indicated by the curvature

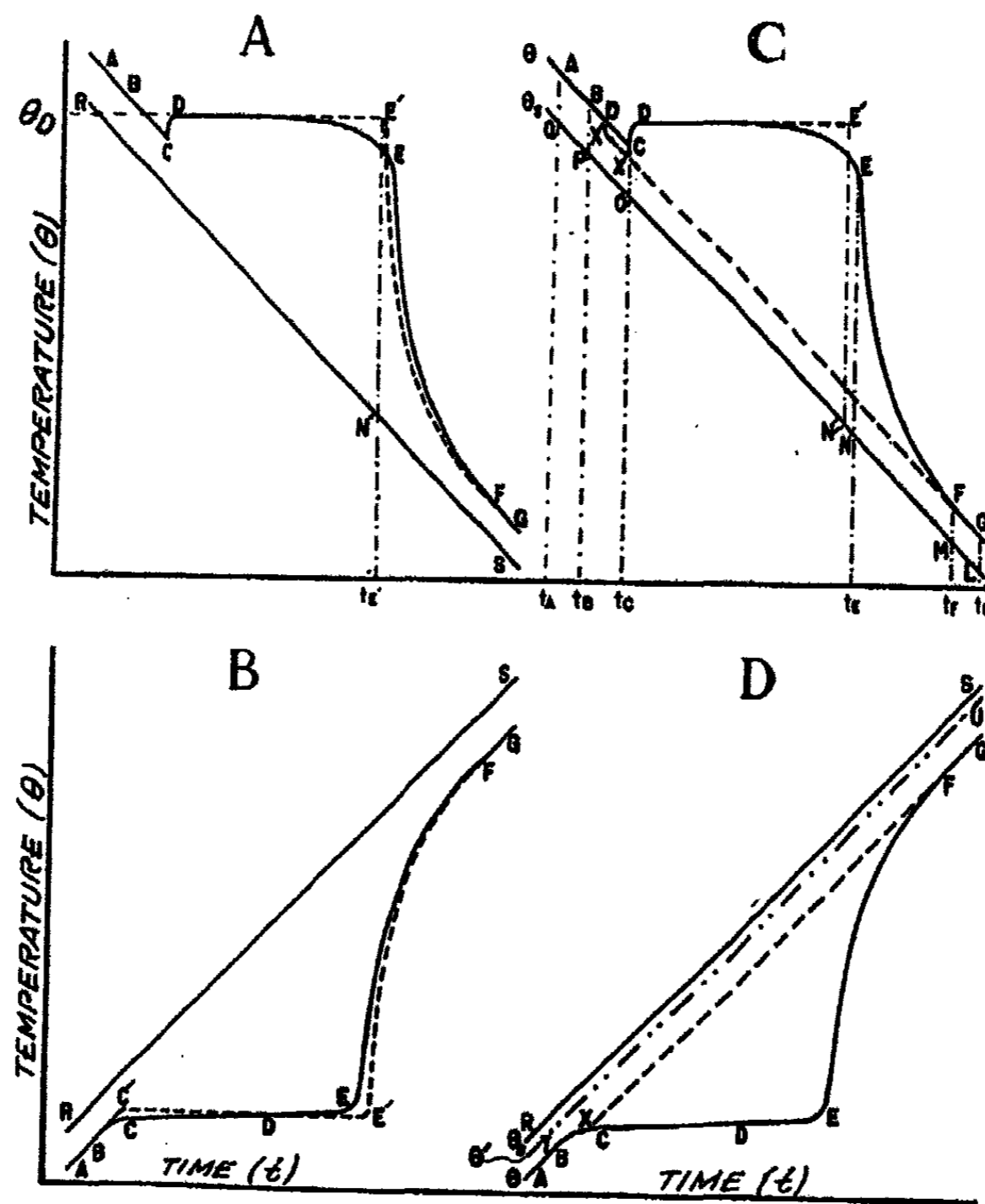


FIG. 2

Typical experimental and limiting time-temperature curves for a substance undergoing change of state under carefully regulated conditions.

of the lines ABC and EFG and to favor uniformity of temperature in the freezing mixture, the temperature of the surroundings may be so regulated that a large thermal head does not exist at any time.

The Regulated Time-Temperature Curve

If the surroundings are cooled or heated at a constant rate, the "ideal" or limiting time-temperature curves of a body changing state are shown in Fig. 2A and B, where the curve RS indicates the change of temperature of the

surroundings with time, and the curve ABC'DE'FG the change of temperature of the body on the basis that there is throughout the run thermal equilibrium (i.e., uniformity of temperature) in the mixture of liquid and solid

In practice, on cooling a liquid at its freezing temperature (Fig. 2A) some degree of undercooling is likely to occur in which case the temperature of the liquid follows the curve ABC; inoculation at C by addition of a seed crystal, or by scratching, induces crystallization and the temperature rises to θ_D , the freezing temperature of the liquid, where it remains until crystallization is complete at the time t_E' . During solidification, the thermal head increases to the value E'N'; this built-up thermal head causes the solid to cool quite rapidly along the curve from E' to F where a steady state between the cooling body and its surroundings is again attained.

This ideal or limiting curve is, however, never completely realized because of lack of thermal equilibrium within the cooling body. For any cooling body, a finite rate of heat loss implies a thermal gradient in the body, which is incompatible with complete thermal equilibrium. In liquids convection currents prevent large thermal gradients¹, but convection becomes less effective as solidification proceeds so that the measured temperature of the body, deviating farther and farther from thermal equilibrium, follows the curve DEF. This curve deviates most from ideality at the point E where solidification is substantially complete, and where heat loss from the center of the body proceeds only by conduction through the solid. Again, a thermal gradient in the body implies that the value of the temperature which is read depends on the position of the thermometer, and this effect appears in the shape of the curve. However, by regulating the rate of cooling and by placing the thermometer properly, one may obtain data which yield curves approaching the "ideal" curve as a limit.

In practice an additional factor prevents realization of the ideal curve. Impurities in a substance which crystallizes out in the pure state lower the melting temperature of the substance; as crystallization proceeds, the concentration of the impurity in the liquid increases, consequently the melting temperature is progressively lowered as along the curve DEF. This effect, which can be calculated, has been used by White to estimate the amount of impurity.

Various attempts have been made to correlate the time-temperature curve of a body with its change in heat content, some being based on reasoning analogous to Newton's law of cooling and others on empirical formulae. Regnault² and Mellecoeur³ have derived specific heats from observations of rate of cooling. Hüttner and Tammann,⁴ Plato,⁵ Schwartz and Sturm,⁶ and Roos⁷ have estimated the heat of fusion of some inorganic salts and metallic

¹ White: *J. Phys. Chem.*, 24, 393 (1920).

² *Compt. rend.*, 70, 664 (1870).

³ *Ann. Chim. Phys.*, (8) 23, 566 (1911).

⁴ *Z. anorg. Chem.*, 43, 215 (1905).

⁵ *Z. physik. Chem.*, 55, 721 (1906); 63, 447 (1908).

⁶ *Ber.*, 47, 1730 (1914).

⁷ *Z. anorg. Chem.*, 94, 329 (1916).

compounds from time-temperature curves. White¹ has discussed some of the errors involved in a radiation method, and has emphasized, as has Roos, the empirical nature of the formulae employed by the foregoing investigators. Hare,² applying Newton's law of cooling, obtained values for the heat of transformation of some polymorphous salts. Roos, by the use of an additional constant in his equation, and Hare by the use of Newton's law of cooling, have developed equations not necessarily limited to a particular apparatus. Andrews, Kohman, and Johnston,³ deriving the equation

$$H_B - H_A = K \int_A^B (\theta_B - \theta) dt$$

have shown that if Newton's law holds, the change in heat content ($H_B - H_A$) of a body in passing from A to B is measured by the properly integrated area between θ and θ_s curves. This method of treatment is distinct from that of previous investigators who used the *length of flat* (i.e., the time of freezing) of the cooling curve as a factor in determining changes in heat content.

The Relation between Heat Content and the Time-Temperature Curve

Notwithstanding the fact that, with the exceptions noted above, the formulae which have been used in the application of radiation calorimetry to the measurement of heat of fusion of transition have been empirical, and applicable only to the apparatus for which they have been designed, there is a theoretical basis for radiation calorimetry which may be deduced from the following considerations:

The heat flow from a body to its surroundings is a function of the temperature of the body θ , that of its surroundings θ_s , and of the nature and extent of the surfaces and the intervening medium. Expressed mathematically

$$dH/dt = f(\theta, \theta_s, a, b, c, \dots) \quad 1)$$

where H is the heat content of the body, t the time and a, b, c, \dots are the factors, just referred to, which affect heat flow.

In a given apparatus the variables other than the two temperatures may be kept constant by the use of the identical set-up; namely, the same container throughout, and by the precaution of always placing the body in a fixed position with respect to its surroundings. This being so, it is only necessary to determine the functional relation fixing the two remaining variables θ and θ_s , and the rate of gain (or loss) of heat. As a first approximation the rate of heat loss may be considered a function of the thermal head, i.e.,

$$-dH/dt = f'(\theta - \theta_s) \quad 2)$$

and, for use within a small range near a definite temperature θ , equation 2 may be approximated to

$$-dH/dt = K(\theta - \theta_s) \quad 3)$$

¹ Am. J. Sci., 28, 485 (1909).

² Phil. Mag., (6) 48, 414 (1924).

³ J. Phys. Chem., 29, 914 (1925).

where K is some constant whose value depends on the nature and dimensions of the apparatus, and on the temperature at which the apparatus is used. Equation 3 should represent closely the loss of heat due to conduction and convection. Even for radiation, which is proportional to $(\theta^4 - \theta_s^4)$ where temperature is measured on the absolute scale, equation 3 expresses the rate of heat loss, for a value of $(\theta - \theta_s)$ ranging up to 9° (which exceeds any observed thermal head) to within 5% at 300°K , and to 3% at 450°K . All measurements of heats were made between 313°K and 421°K , within the above limits.

As a test of equation 3 the cooling of mercury in a preliminary apparatus was observed. Where C is the specific heat of mercury we may write

$$dH = Cd\theta$$

if there is no change of state involved. Substituting in equation 3, and placing $q = K/C$ we have

$$-d\theta/dt = q(\theta - \theta_s) \quad 4)$$

which is an expression of Newton's law of cooling. It is evident that q is constant only when C is constant, and the utilization of equation 4 is limited by that condition. Since the change in specific heat of mercury over a temperature range (20° to 50°C) greater than that used in testing equation 3 is less than 1%, q in equation 4 may be considered constant, and accordingly, by integration equation 5 is obtained.

$$-\log(\theta - \theta_s) = q/2.3 t + I \quad 5)$$

TABLE I
Application of Newton's Law of Cooling
Rate of Cooling of Mercury in a Preliminary Apparatus.

| Time (Min.) | Temperature* (Microvolts) | Temperature Head ($\theta - \theta_s$) | Log ($\theta - \theta_s$) | Decrement in log ($\theta - \theta_s$) per minute |
|-------------|---------------------------|------------------------------------------|-----------------------------|-----------------------------------------------------|
| 0 | 1850 | 913 | 2.960 | |
| 1 | 1580 | 643 | 2.808 | 0.152 |
| 2 | 1405 | 468 | 2.670 | .138 |
| 3 | 1263 | 326 | 2.513 | .157 |
| 4 | 1168 | 231 | 2.364 | .149 |
| 5 | 1101 | 165 | 2.218 | .146 |
| 6 | 1053 | 117 | 2.068 | .150 |
| 7 | 1019 | 83 | 1.919 | .149 |
| 8 | 995 | 59 | 1.771 | .148 |
| 9 | 978 | 42 | 1.623 | .148 |
| 10 | 967 | 31 | 1.491 | .132 |
| 11 | 958 | 22 | 1.342 | .149 |
| 12 | 952 | 16 | 1.204 | .138 |
| 13 | 947 | 11 | 1.041 | .163 |
| | | | Mean decrement | .148 |

* Copper-constantan thermoelement. One degree centigrade is about 40 microvolts.

As the last column of Table I shows, the decrements of $\log (\theta - \theta_s)$ per unit time are constant for values of the thermal head ranging from 913 to 11 microvolts* (23° to 0.25°C). The greatest deviation from the mean (last column) occurs where the greatest error in reading $(\theta - \theta_s)$ occurs, i.e. where θ is changing rapidly, or where $(\theta - \theta_s)$ is small. Andrews, Kohman and Johnston¹ tested Newton's law in a different but similar apparatus using naphthalene in a glass tube as the cooling body with results similar to those in Table I. Since the thermal head encountered in the experimental work lies between 350 and 10 microvolts, well within the limits of the above test, Table I shows that, within useful experimental limits, equation 3 may be used to express the rate of heat loss of a body. Accordingly, for small thermal heads near a given temperature, K may be regarded as a constant characteristic of the apparatus used; it is a measure of the rate of heat loss per degree of thermal head, and is independent of the nature of the body supplying the heat so long as the conditions mentioned above, concerning the container and its position in the apparatus, are maintained. However, since the rate of heat loss by radiation depends on the absolute temperature of the radiating body as well as on the thermal head, and since the rate of heat loss by conduction and convection may be affected similarly though to a lesser extent, the value of K is to some extent dependent on the temperature at which the apparatus is used. This question, which enters only when the apparatus is used at different temperatures, will be discussed later.

As suggested above, time-temperature curves in practice deviate somewhat from the ideal or limiting curves; therefore, all deductions will be based on such typical curves (Fig. 2C and 2D) as are encountered in practice. Since a specific transformation must be chosen if detailed description is to be given, the transformation discussed will be the freezing of a pure liquid to a crystalline solid. Now a substance between two points such as A and B on the curve ABCDEFG (Fig. 2C) undergoes a change of heat content which may be evaluated as

$$- \int_A^B dH = K \int_{t_A}^{t_B} (\theta - \theta_s) dt$$

| | |
|-----------|--------------------------------------|
| or | $H_A - H_B = K \text{ area ABPQ}$ |
| Similarly | $H_C - H_F = K \text{ area CDEFMOC}$ |
| and | $H_F - H_G = K \text{ area FGLM}$ |

$H_A - H_B$, $H_F - H_G$, and $H_C - H_F$ represent respectively the change of heat content of the specimen due to its specific heat as a liquid; that due to its specific heat as a solid; and that due to two factors, (1) the heat of fusion of the specimen, and (2) the heat evolved by the solid in cooling from E to F.

Since the heat of fusion is to be measured as a distinct quantity apart from the remaining heat content of the specimen, the precise area under the

* A copper-constantan thermoelement was used; 1°C equals 40 microvolts.

¹ Loc. cit.

curve ABCDEFG which measures the heat of fusion must be determined. Three possibilities which present themselves are:

1) The area CDENOC. Here the difficulty of determining the length of flat DE over which freezing proceeds, enters, for, as mentioned above, the temperature of the freezing mixture falls off as crystallization nears completion. If there were no falling off, the area measured would be CDE'N'OC (Fig. 2C). In all previous attempts to measure such heats by radiation calorimetry the heat effect was evaluated as some function of the length of flat DE; as may be seen from the typical experimental curve, such procedure involves uncertainty in the choice of the portion of the curve to be considered as the "flat," and the choice necessarily is somewhat arbitrary. A further objection to this method is that the area due to any heat loss by the container of the specimen and its supports is included in the area measured; for, while it is true that there is little or no temperature change in the specimen during freezing, this need not be true of the container and its supports. Lastly, the method would require the accurate measurement of the *effective* temperature of the surroundings, i.e., the temperature at that portion of the surroundings which exchanges heat with the cooling body, and not merely some temperature which differs from this *effective* temperature by some constant quantity.

2) The area CDEFC which is bounded on the lower side by the straight line from C to F. This method, however, is incorrect if there is any appreciable difference between the specific heat of liquid and of solid, for the specimen which cools from E to F is solid, and not a mixture of liquid and solid as the choice of the line EF as boundary of the area implies. The heat due to the specific heat of the *solid* is therefore the correct heat to be deducted to yield the heat of fusion.

3) The area XCDEFX bounded by the line FX. This is the correct area if FX is constructed parallel to MO as the extension of FG, the part of the curve representing the cooling of the solid. The area XFMO, then, represents the heat given off by the solid in cooling from D to F. There may be a slight error in not correcting for undercooling when the specific heats of liquid and solid are different; in this event freezing begins at θ_C instead of at θ_D , and the liquid in cooling this extent has lost $C_1(\theta_D - \theta_C)$ calories. If there is no undercooling, it is the solid which cools from the temperature θ_D to θ_C and the difference between the two cases is $(C_1 - C_s)(\theta_D - \theta_C)$ calories. Since, in practice, the extent of undercooling is one degree centigrade or less, $(\theta_D - \theta_C)$ may be taken as unity, and the difference becomes $(C_1 - C_s)$ calories as a maximum. This quantity is represented graphically by the area CXX'D. The data of Andrews, Lynn and Johnston¹ indicate that the error arising from neglect of this factor may range from 0 to 0.5%. The correction indicated above may be made whenever necessary.

For the case of the transition of a crystalline solid, there may, or may not be undercooling in the cooling curve. In the heating curve (Fig. 2D) for the

¹ J. Am. Chem. Soc., 48, 1274 (1926).

melting of a pure crystalline solid, there is no corresponding superheating; the same is frequently true for the transition of solids from one crystalline form to another. The area measuring the heat of fusion or transition may be derived, by a treatment similar to the above, as the area XEF, bounded by FX, the prolongation of FG which here represents the curve for the liquid.

The area measuring the heat of fusion or transition can be evaluated if $(\theta - \theta_0)$ is known as a function of t ; but it is more easily determined graphically since the time-temperature curves may be plotted on coordinate paper, and the squares in the appropriate area counted. Then, if L is the molal heat of fusion or transition, the heat set free in any mass of n mols is nL calories and the general expression becomes

$$nL = K \text{ area CDEFXC}$$

K may be evaluated if a similar substance of known mass, n' mols and known heat of fusion L' is placed in the apparatus and the "heat of fusion" area determined. As was mentioned above the "apparatus constant" K may change with changing temperature owing to modification of the mechanism of heat transfer. Such variation of K with the temperature can be determined by the use of a series of calibrating substances which melt at different temperatures. The values of K , derived in this manner, plotted against the temperature, should yield a smooth curve, so that in practice the value of K at any temperature may be read from this curve.

As was shown, by experiment, equation 3 is valid for the apparatus used, and it has accordingly been used in the interpretation of the results. The method is in fact more general than was assumed above, for it would be applicable in apparatus for which equation 3 is not valid so long as the rate of heat loss (gain) is some function of the thermal head, i.e., so long as equation 2 holds. For, if the masses of two specimens be so chosen that the areas representing the heats of fusion are equal, the quantities of heat evolved will be equal, regardless of the nature of the unknown function, and accordingly, the relative heats of fusion may be obtained. In this case, also, the unknown function may change with temperature, but if this occurs in a regular manner, as is to be anticipated, the change of area per calorie with changing temperature may be determined by the use of substances of known heat of fusion and varying melting temperature for the calibration. The value at any temperature may therefore be read from the smooth curve passing through such experimentally determined points. In practice, then, it is desirable to deal with such quantities of the several substances as yield substantially equal "heat of fusion" areas, for this procedure obviates to a large extent any question as to the strict applicability of equation 3.

Application to Specific Heats

Objections to the use of the θ , curve as a boundary for measuring heats have a special significance when the radiation calorimeter is applied to the determination of specific heats. This follows, in part, from the use of material objects as container and supports for the specimen. The "specific heat"

area under the time-temperature curves can be evaluated by running the apparatus empty, i.e., with the identical set-up except that the specimen itself is omitted. The thermal head in such an event will be $(\theta' - \theta_s)$ (Fig. 2D), and the thermal head due to the specimen will be $(\theta - \theta')$. If, then, θ' is substituted for θ_s in all previous equations, correction will have been made for container and supports.

Again, heat loss from (to) the container is governed in part by the rate of transfer of heat to (from) the radiating surface by the specimen, i.e., to the completeness of thermal equilibrium within the container. This factor is of little or no importance when the specimen is liquid, for convection currents then insure good heat distribution, but it does enter when the specimen is solid and heat distribution can proceed solely by conduction. For this reason, in any determination of specific heats, the value of K should be obtained for both states of the substance used for calibration. It is furthermore to be noted that substances used in calibrating the apparatus should be similar in thermal properties to those whose heats are to be determined.

The foregoing discussion of the interpretation of the thermal head in specific heat determinations implies that the recorded thermal head is the effective thermal head, i.e., the actual temperature difference which controls the flow of heat between the specimen and its surroundings. If this condition is to be fulfilled, the temperature of the radiating surface of the specimen and surroundings must be measured. If the thermometer for the surroundings is not placed in this position but in some other fixed position, it may indicate a temperature which differs by a constant amount from the temperature at the radiating surface. Thus the actual temperature read may be indicated by the curve RS (Fig. 2D) whereas the temperature of the "radiating surface" of the surroundings would be represented by the curve TU . Although this consideration is of prime importance for the determination of specific heats, it does not affect the determination of heats of fusion and transition so long as there is a constant difference between the effective temperature of the surroundings and the observed temperature, i.e., so long as the curves RS and TU (Fig. 2D) remain parallel.

Apparatus

Any apparatus used in the application of the calorimetric method outlined above must fulfill the necessary conditions which may be summarized as follows:

1. The substance under investigation must be placed in a container which is constant with respect both to the extent and nature of its radiating surface, and to its position with respect to its surroundings. The nature of the radiating surface of the surroundings must likewise remain unchanged. Any departure from these conditions would change the apparatus constant K .
2. The temperatures of the radiating body and its surroundings, or strictly comparable quantities, must be accurately measured. Since it is the difference between these temperatures which enters into the equation for calculating change of heat content, a differential thermoelement may be used to measure this difference directly.

3. Attainment of thermal equilibrium in the radiating specimen should be rapid compared with the heat exchange with the surroundings. Stated in other terms, this means that the effective thermal head should be large compared with temperature differences within the specimen. Under these conditions the largest possible thermal head is measured, with a corresponding maximum of percentage accuracy for a definite precision in the measurement of the thermal head. Since the substances we proposed to use, viz., organic compounds and inorganic salts, are poor heat conductors, definite

TABLE II
Thermal Conductivities from Landolt-Börnstein Tabellen
K

| | | |
|-----------------|---------|--------|
| Naphthalene | 0.00095 | (35°) |
| Glass (average) | 0.002 | |
| Platinum | 0.173 | (100°) |
| Copper | 0.92 | (100°) |

Values from the Landolt-Börnstein Tabellen.

restrictions are imposed on the size and shape of the container for the specimen. Table II gives the coefficients of heat conductivity of several substances. If the liquid is freezing, the ring of crystals which forms around the wall of the tube delays the passage of the heat from the axial portion of the tube to the peripheral portion where heat loss to the surroundings occurs. The retarding process here may be either the rate of crystallization, or the conduction of the liberated heat through the solid to the walls of the container. If a solid is melting, the liquefaction first occurs at the walls of the container resulting in a liquid medium for the transfer of heat to the surface of liquefaction. The rate of melting is here likely to be the slow process. For transitions in the solid state the rate of transition is more likely to be the dominating factor than is the rate of crystallization or of melting in the change solid \rightleftharpoons liquid.

An attempt to combine the principles enumerated above with a maximum ease of manipulation and replacement resulted finally in the apparatus outlined in Fig. 3 and described below: *A* is a pint-sized, silvered Dewar flask. *B* is brass tube 5.5 cm. in diameter, 15 cm. long and 0.5 cm. in wall thickness with a brass plug 1.3 cm. in thickness pressed into the bottom. The tube is wrapped with thin mica sheets over which is wound a heating coil *a* of nichrome ribbon—(about 28 ohms resistance). A coating of waterglass aids in holding the coil in place and asbestos paper wrapped around the whole serves as a heat insulator for the tube and a protector for the Dewar flask. The tube rests on shredded asbestos *b* on the bottom of the Dewar flask, cotton *c*, over the open end of the tube, reducing erratic thermal changes; *C* is a copper cylinder split into halves lengthwise and milled to fit into the brass tube; it is 12.7 cm. in length and 4.5 cm. in diameter with a 1.9 cm. axial hole extending from the bottom to within 3.2 cm. from the top, from which

point a hole 0.56 cm. in diameter extends to the top of the cylinder. The whole is silver-plated to minimize corrosion. Resting in the upper hole at the top is a tube of thin glass *D* to which is sealed a platinum capsule *E* 2.5 cm. in length, 0.5 cm. in diameter, with a re-entrant tube 0.5 cm. long and 0.05 cm. in diameter sealed into it; the over-all length of the platinum-glass capsule is 10.8 cm.

F is a differential element of No. 40 B & S gauge copper and No. 36 constantan, one junction of which is at *d* packed into the re-entrant tube of the platinum capsule with mat gold* which insures good thermal contact. The other junction is at *e*, the constantan being the wire from *d* to *e*. Both leads to the potentiometer are held in place in the copper block by means of brass strips such as *f*. *G* is a thermoelement soldered into the top of the block at *g*. The readings of the thermoelements *F* and *G* are taken with a White double potentiometer. The apparatus, including switch-board, galvanometer and potentiometer, is shielded by an equipotential shield after the recommendations of White,¹ and single-pole knife switches are used throughout to prevent any possible erratic effects. Since alternating currents frequently create induction currents which affect the potentiometer galvanometer, the heating is done with direct current. Under experimental conditions the current flowing in the heating coil *a* was on the order of 0.5 amperes; the potential across the two ends of the wire was therefore about 15 volts.

Two platinum capsules were used; the second, designated hereafter as Tube 2 is described; the first (Tube 1) was of somewhat different dimensions. It has the same diameter as Tube 2 but was 2 cm. instead of 2.5 cm. in length, and its re-entrant tube was 1 cm. in length and 1 mm. in diameter instead of 0.5 cm. in length and 0.05 mm. in diameter. In both cases the length of the platinum-glass tube over-all was 10.8 cm., but the radiating surface, and the length of the path of heat conduction up the walls of the glass tube differed. In the experimental data given below, the tube used is therefore designated.

* Obtained from a dental supply house.

¹ J. Am. Chem. Soc., 36, 1856, 2011 (1914).

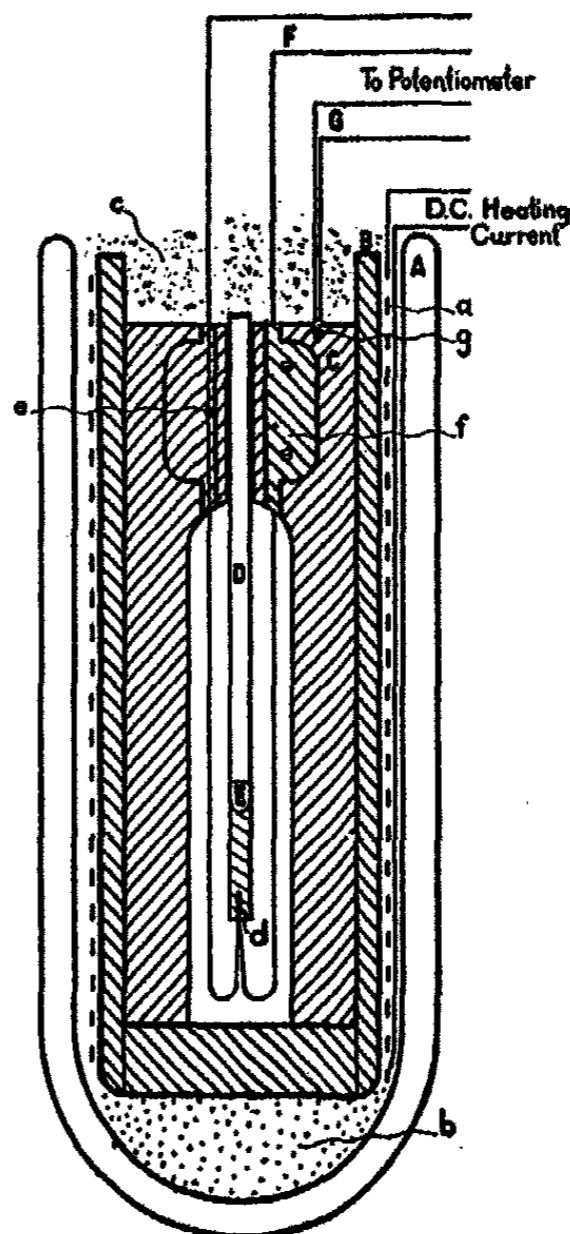


FIG. 3
Diagram of the Radiation Calorimeter

In some preliminary experiments tubes wholly of glass were used in place of the platinum-glass tube as container for the specimen. In these tubes, the path of conduction up the wall of the tube does not remain constant as the amount of specimen is varied; with the platinum-glass tube conduction along the wall of the tube is limited by the conductance of the glass and therefore does not vary with the level of the substance in the attached metal capsule. The latter tube also obviates the use of a central thermoelement, eliminating the attendant difficulties enumerated below.

Experimental Procedure

The desired amount of specimen is weighed into the platinum capsule *E*, (Fig. 3) and melted down to form a solid mass. If the crystals are not melted down several times during a filling, the loose crystals extend into the glass tube *D* and stain it as they melt; for reproducibility it is necessary that *all* the specimen be in the platinum capsule. The glass tube supporting the latter is placed in its proper groove in the one half of the copper cylinder *C* and one junction of the differential element is inserted in the re-entrant tube of the platinum capsule as shown at *d*, where it is tamped into position with mat gold. The other junction of the differential element has previously been soldered at *e*. The other half of the copper cylinder is now placed in position and fastened to the first by screws, and the whole inserted in the brass tube *B*. At first the junction at *d* was left undisturbed when specimens were changed, but the most recent procedure is to remove the element at *d* and determine the weight of specimen used (about 0.35 gram) by the direct weighing of the tube *D-E*, for it is believed that greater reproducibility is obtained by this procedure than by an attempt to determine the weight of specimen by indirect weighing. In the latter case, a tube must be inserted in *D* through which the specimen must be poured if contamination of the walls of *D* is to be avoided, and the possibilities of a loss of material are considerable.

The electromotive force of the thermoelement is read to one microvolt; greater precision is possible, but the entrance of greater errors from other sources has rendered it futile. The temperature of the copper block is indicated by the element *G* so that by suitable regulation of the current through the heating coil *a* the "surroundings" may be heated or cooled (within certain limits) at any desired rate. The differential element *F* indicates the thermal head between the specimen and its "surroundings." For any transformation investigated, readings of the element at definite time intervals are recorded from a time when there is a steady state between the temperature of the specimen and its surroundings (i.e., when the element *F* shows a constant reading) before the transformation, to a corresponding time after the transformation. The rate of heating (or cooling) of the copper cylinder *C* finally adopted was 10 microvolts (about 0.2°C) per minute. Under these conditions the time between steady states before and after transformation was, for the size of specimens used, about 60 minutes, and the temperature interval involved was 600 microvolts or about 13°C.

Since the differential element indicates directly the difference in temperature which is sought, the experimental results are most easily utilized if the thermal head ($\theta - \theta_0$) is plotted against elapsed time as in Fig. 5 in which the letters have the same significance as in Fig. 2C. The sign of the thermal head is, of course, dependent on whether the curve is a heating curve or a cooling curve just as is the sign of the heat of fusion. The boundaries of the heat of fusion area in Fig. 5 are the same as those discussed in connection with Fig. 2C and D. The experimental curves were plotted on millimeter paper, the time as abscissa, one centimeter representing $1\frac{1}{2}$ minutes, and the thermal head as ordinate, one centimeter representing 25 microvolts. A larger scale would be desirable if the reproducibility of the method is increased, but for the degree of reproducibility obtained the scale proved satisfactory. In general, for heats of fusion, the area for the specimens used ranged from 140 to 230 square centimeters. The method adopted for determining the desired areas was the counting of squares, which for approximately straight portions of the curve can best be accomplished by the reading of ordinates at definite intervals. Gross errors can in the main be eliminated by uniformity in the plotting of the curves and in the estimation of the areas, for if two curves are similarly plotted in a given space, any difference in their areas can be quickly estimated. With this procedure, the limiting factor is not the estimation of the total area under the curve, but the estimation of the precise area to be deducted as the "specific heat" area. This question will be discussed in connection with the actual experimental work.

The Experimental Time-Temperature Curve

Before the experimental curves are examined, it is well to review some of the principles involved. It is of importance to realize that for poor thermal conductors and for rapid rates of heating and cooling the slope of the curve obtained depends on the position of the thermometer in the specimen. In the case of the time-temperature curve for the determination of a freezing or melting temperature, it is customary to insert the thermometer in the center of the specimen where it will be protected from the surroundings and where, under favorable conditions it will indicate the true melting or freezing temperature. However, it follows from the theoretical discussion that, for purposes of calorimetry, the important temperature is not that at which the specimen undergoes transformation, but that at which the heat is radiated to (or from) the surroundings. If the rate of heating or cooling is slow, this distinction is not important for specimens of good thermal conductors such as metals; it is, however, of importance for poor thermal conductors such as organic compounds or inorganic salts. For the latter, the difference in temperature between the outside and the axial portions of a specimen does not remain constant, and it is evident that the curve representing the temperature of the central part of the specimen and that representing the temperature of its outer surface are the most widely divergent of a series of possible curves. Because of this difference, the temperature of the wall of the container does not remain constant as freezing or melting occurs. Tube 1

shows a better *flat* than Tube 2, for in the former the thermoelement was more nearly in the center of the specimen. The thermoelement in Tube 2 indicates the temperature of the surface more exactly.

As a preliminary to the discussion of the curves obtained with the final apparatus, some of the curves observed with the use of a central thermo-

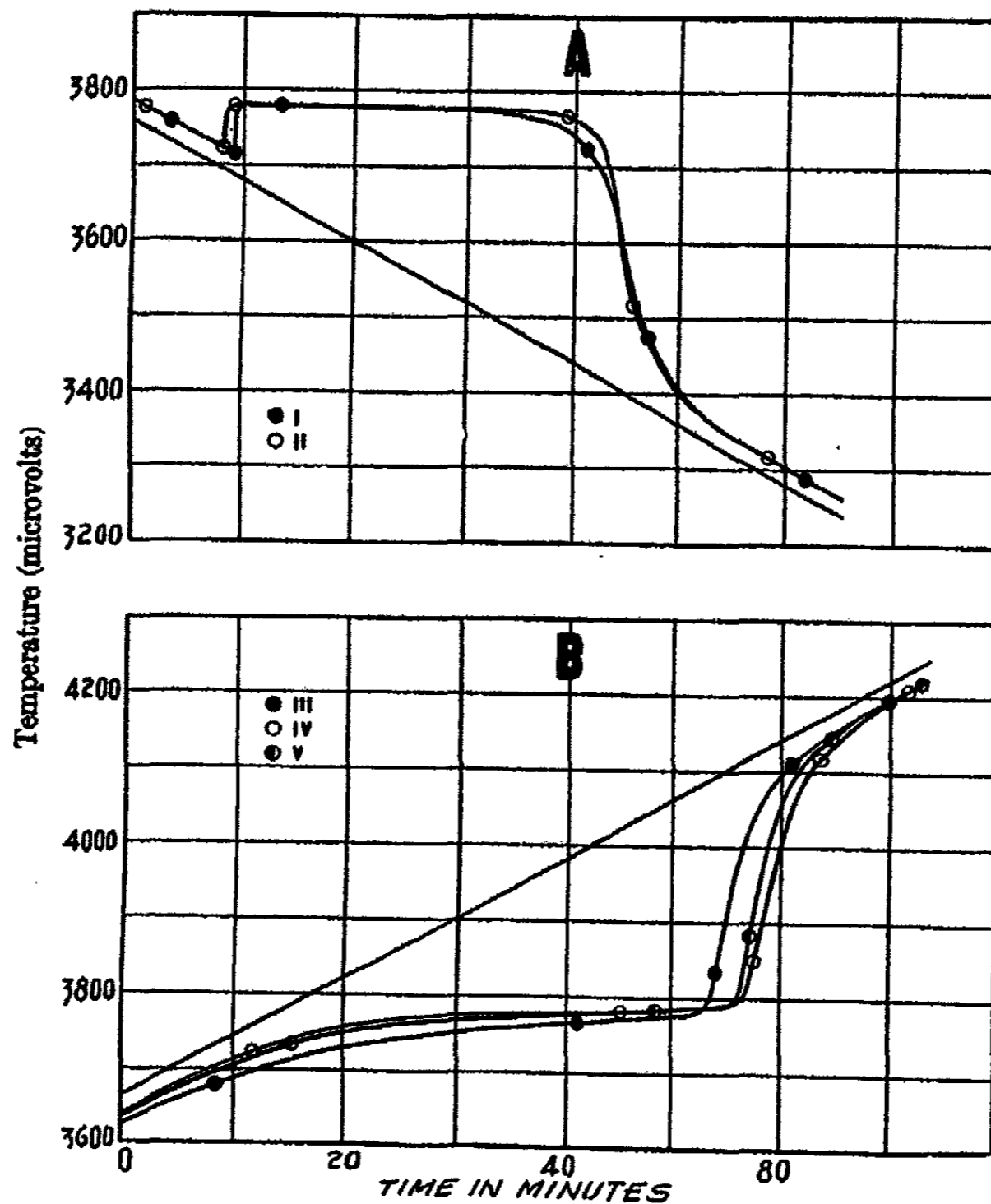


FIG. 4

- I Cooling Curves Nos. 33 and 35
- II Cooling Curves Nos. 38, 39 and 42
- III Heating Curve No. 32
- IV Heating Curve No. 34
- V Heating Curve No. 36

- o. 378 g.m-dinitrobenzene
- o. 373 g.m-dinitrobenzene
- o. 378 g.m-dinitrobenzene
- o. 378 g.m-dinitrobenzene
- o. 378 g.m-dinitrobenzene

element in a preliminary apparatus will be analyzed. Fig. 4A shows two cooling curves, Curve I representing cooling curves #33 and #35, and curve II #38, #39, and #42; any deviations of the several curves from the representative curve drawn are too small to be shown on such a scale. It will be noted that curve I for the larger specimen (0.378 g.) has a smaller heat of fusion area than Curve II representing the smaller specimen (0.373 g.); and that the

shape of the curves is different owing to differences in position of the element. Fig. 4B shows curves III, IV and V which represent, respectively heating curves #32, #34, and #36 for the same specimen as curve I (Fig. 4A); heating curves for the same specimen as curve II showed similar variations, therefore are not reproduced. It is at once evident that the heating curves do not show the same reproducibility as cooling curves; indeed the melting temperatures as indicated by the several curves seem to differ. Although the "heat of fusion" areas for the heating curves show better agreement among themselves than might be suspected from the appearance of the curves, in general, with the central thermoelement, the "heat of fusion" areas obtained from heating curves and from cooling curves do not show good agreement.

TABLE III

A Comparison of Heating Curves and Cooling Curves observed with a Central Thermoelement; substance *m*-Dinitrobenzene

| Curve No. | Wt. of Specimen gms. | Type of Curve | Heat of Fusion Area (Arbitrary Units) | Area per Gram Heating Curve | Area per Gram Cooling Curve |
|------------|----------------------|---------------|---------------------------------------|-----------------------------|-----------------------------|
| 1st Series | | | | | |
| 32 | 0.378 | Heating | 226 | 598 | |
| 33 | " | Cooling | 237 | | 627 |
| 34 | " | Heating | 229 | 606 | |
| 35 | " | Cooling | 237 | | 627 |
| 36 | " | Heating | 231 | 611 | |
| 2nd Series | | | | | |
| 38 | 0.373 | Cooling | 242 | | 649 |
| 39 | " | " | 243 | | 651 |
| 40 | " | Heating | 231 | 620 | |
| 41 | " | " | 245 | 657 | |
| 42 | " | Cooling | 243 | | 651 |

After some cooling curves were run with the final apparatus, heating curves were again tried, and it was found that with this apparatus heating and cooling curves agreed as well with one another as among themselves. (Cf. Tables IV and V.) This is an indication that in this case the measured thermal difference between the radiating surface of the specimen and that of the surroundings was very nearly the effective thermal head. The decision as to whether heating curves or cooling curves shall be run depends on the following factors:

Since it is desired to have a uniform rate of cooling or heating at different temperatures, the maximum rate of cooling desired at the lowest temperature must equal or exceed this constant rate. If the apparatus is so thermally isolated by a Dewar flask as to give a slow rate of cooling at high temperatures the rate of cooling near room temperatures becomes exceedingly slow. It is accordingly difficult to maintain a constant rate of cooling over a range

of temperatures. This difficulty disappears if heating curves are used, for the heating current can be so regulated as to give the desired rate of heating at any temperature within the limits of the apparatus.

A second factor relates to the possibilities of undercooling or superheating. In general, for a liquid-solid transformation, undercooling of the liquid occurs in the absence of crystals whereas superheating of the solid is unusual. For solid-solid transformations, the rule is not so invariable, for slow rates of transformation are frequent, resulting in the persistence of a crystal form far beyond the temperature range in which it is stable. Again, the rate may differ with the direction in which the transformation occurs. It is apparently common for the transition of a low-temperature form to a high-temperature form to proceed more readily than the reverse transition; as an example mercuric iodide may be cited, the transition of the red low-temperature form to the yellow high-temperature form proceeding readily without superheating at the transition temperature (127°C), but the reverse transition showing the phenomenon of undercooling so that the yellow form may persist at room temperature.

A third factor relates to the possibility of irreversibility. A reaction may occur in the liquid state which does not occur in the solid state; under such conditions it might be possible to run a heating curve, though not a cooling curve. Irreversibility, on the other hand, may be due to the condition of the solid, as in the case of the metals where "quenched" and "annealed" specimens are known to have different properties. A cooling curve in such a case would show only the heat of fusion of the annealed solid to the liquid; a heating curve, however, could conceivably be used to determine the heat of fusion of a quenched as well as of an annealed specimen.

A fourth factor is the degree of certainty of extrapolation of the "specific heat" boundary. Although it is preferable to have curves which approach the "ideal" curve as nearly as possible, deviations from such a limiting curve do not have as great effect on the heat of fusion area as the shape of the curve might lead one to suspect, if the extrapolation is carried out properly. The effect of impurity on the time-temperature curve has been discussed. The effect on the heat of fusion area, however, depends only on the actual amount of heat involved in such transformation which proceeds outside the temperature limits covered by the curve, providing that the impurity causes no large heat effect of another kind. If the amount of impurity is small and forms a nearly ideal solution, in the liquid phase, with the substance under investigation, the amount of material melting or freezing outside of the temperature limits of the experiment is small. An advantage of the heating curve over the cooling curve appears here, for in the former, after transformation is complete, the extrapolation of the "specific heat" boundary of the specimen is done from the liquid curve on which the effect of the impurity is slight; in the latter, the extrapolation is done from the solid curve, the slope of which is affected by the freezing of the impurity.

These considerations led finally to the utilization of the heating curve as the best fitted for the present investigation. The constancy of the "ap-

paratus constant" K will, however, be discussed for the cooling curve as well as for the heating curve. A typical cooling curve for Tube 1 is shown in Fig. 5A, and typical heating curves for Tubes 1 and 2 are shown in Fig. 5B.

The Apparatus Constant K

As indicated previously the apparatus constant K is defined by the equation $L = KA$, where A = heat of fusion area for one mole. If the curves are plotted on a uniform scale, the unit area being the square centimeter, K

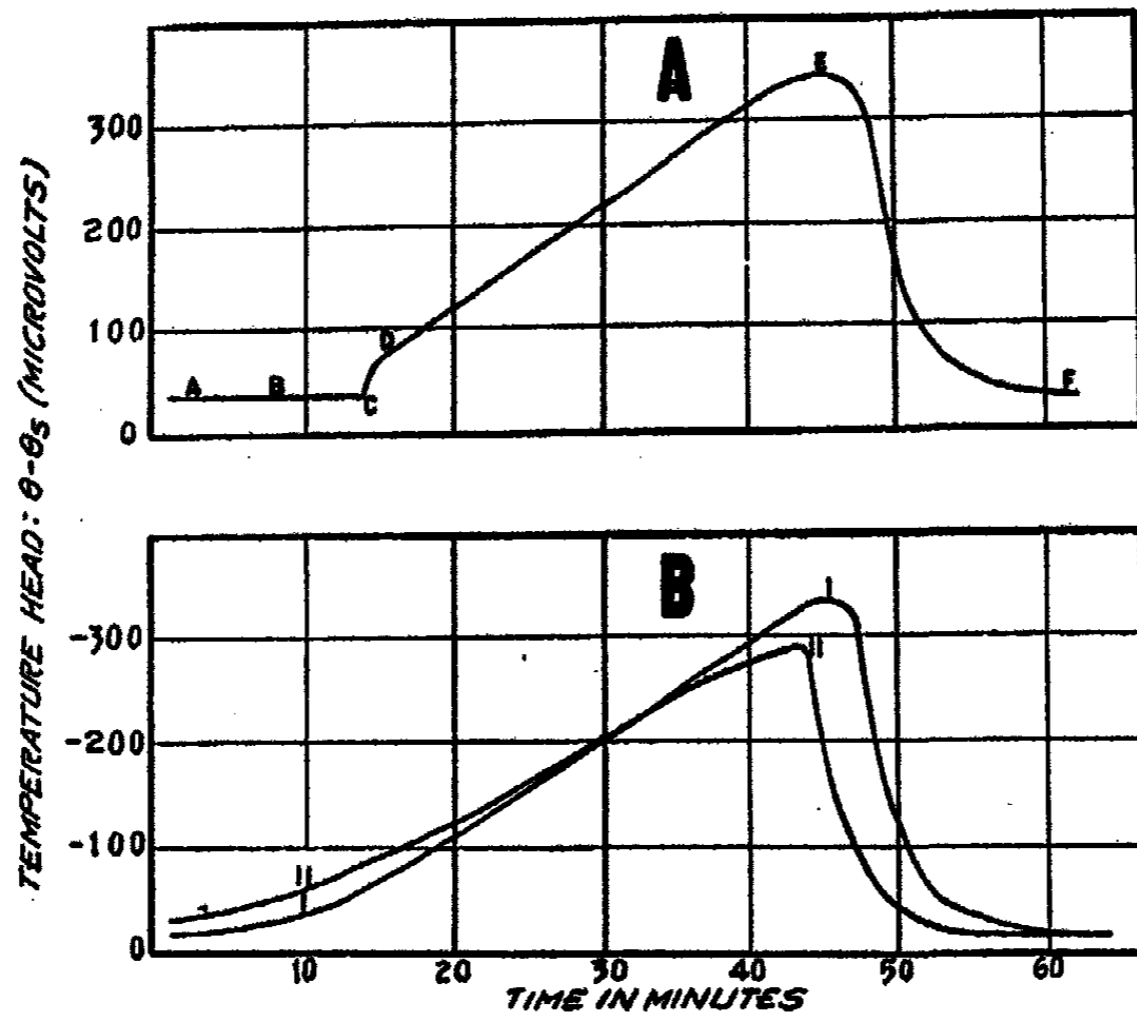


FIG. 5

A.—Cooling Curve No. 102 (Tube 1) 0.304 g. *m*-nitraniline.
 B.—I Heating Curve No. 125 (Tube 1) 0.306 g. *m*-nitraniline.
 II Heating Curve No. 190 (Tube 2) 0.316 g. *m*-nitraniline.

measures the number of calories per square centimeter, for the particular set-up. As long as constant conditions are maintained there should be no deviations in its value, but such conditions no longer obtain rigidly when the apparatus is used at a series of different temperatures. From a consideration of the experimental procedure, it would be expected that the apparatus constant will vary somewhat with the temperature. Three effects must be considered:

1. The change in the constant due to the conditions of heat transfer. Some of the heat is transferred by the air which surrounds the specimen. The constant of thermal conductivity of air between 0°C and 100°C ranges from 5.66 to 7.19×10^{-5} , or an increase of 27% in the hundred degree interval. The rôle played by air as a conductor is slight, but the increased conductivity may appear in increased loss by convection, for the increase of viscosity of a

gas with temperature near room temperature is slight. The loss of heat by radiation changes still more rapidly, for, with a temperature difference of 5°C between the radiating bodies, an increase in temperature from 400° to 500° Kelvin nearly doubles the rate of heat loss. The loss of heat by conduction along the glass tube varies by about 5% for a hundred degrees. Since the relative heat loss by these various means is unknown, a quantitative calculation of their effect on K cannot be made, but the general effect is to increase the rate of heat loss at the higher temperatures.

2. The effect on the constant due to the recording of the thermal head ($\theta - \theta_0$) in microvolts instead of degrees centigrade. In the temperature interval of 2000 to 7000 microvolts (which corresponds to 50° to 156°C) the number of degrees centigrade per hundred microvolts changes from 2.33 to 1.97*, or a decrease of 15%. At the higher temperatures, therefore, the effect is to increase the area under the curve for a definite difference in temperature since the recorded difference in microvolts will be greater. This effect, then, is to decrease K .

3. The effect of the change in rate of heating or cooling due to the variation of degrees centigrade per microvolt with the temperature, since a rate of 10 microvolts per minute was maintained. The effect should be small or negligible if the rate is not so rapid as to cause serious thermal differences in the specimen; this appears to be true, for a run with a rate of heating of 5 microvolts per minute did not show a great effect on K .

It will be observed that the first and second effects discussed exert opposite influences on the apparatus constant, the first tending to increase and the second to decrease K . From the data in Tables IV and V, it can be seen that there is no uniform trend of the constant as higher melting temperatures are approached; the two effects tend so to compensate one another that the temperature correction is for our particular apparatus less than the experimental error.

The assumption implicit in the previous discussion is that no great errors in the values of the heat of fusion of the substances used in the calibration of the apparatus, (i.e., in the determination of the apparatus constant) exist, and a check on the accuracy of the values lies in the smoothness of the curve representing the values of K based on those heats. The published values of the heat of fusion of organic compounds are not all reliable, with the result that, if they are used in calibration, one can not be certain whether apparent deviations in the value of K are due to experimental error, or to the use of erroneous heats of fusion as standards. The values of Andrews, Lynn and Johnston for the heat of fusion of some organic compounds appeared to yield consistent results and they are accordingly used exclusively in the evaluation of the apparatus constant. Since the value of K is dependent on the size and kind of container used, there is a set of values for each of Tubes 1 and 2; but as will be seen, they give consistent results when applied to phenol and benzophenone.

*Copper constantan element. "International Critical Tables," 56.

TABLE IV
Data on the Apparatus Constant K obtained from Cooling Curves

| Substance | Published M. P. °C | Tube I *Heat of Fusion cal/mol | Curve No. | Wt. of Specimen (gms) | Heat of Fusion Area (A) (cm) ² /mol | K cal/cm ² |
|--------------------------|--------------------------|-----------------------------------------|--------------|-----------------------------|---------------------------------------------------------|----------------------------|
| <i>m</i> -dinitrobenzene | 90 | 4150 | 84 | 0.327 | 758 × 10 ³ | 0.0547 |
| | | | 85 | " | 753 | .0551 |
| | | | 86 | .394 | 741 | .0560 |
| | | | 87 | " | 751 | .0553 |
| | | | 89 | .340 | 774 | .0536 |
| | | | 90 | " | 790 | .0525 |
| | | | 91 | " | 790 | .0525 |
| | | | 92 | .401 | 778 | .0533 |
| | | | 97 | " | 771 | .0538 |
| | | | 108 | .334 | 760 | .0546 |
| | | | | Mean | .0541 | |
| <i>m</i> -nitraniline | 112 | 5660 | 101 | .304 | 1052 | .0538 |
| | | | 102 | " | 1057 | .0535 |
| | | | | | Mean | .0536 |
| <i>o</i> -dinitrobenzene | 117 | 5460 | 103 | .333 | 966 | .0565 |
| | | | 104 | " | 974 | .0561 |
| | | | | | Mean | .0563 |
| | | | | MEAN | .0544 | |

Average deviation from mean 0.0011 ; 2.0%

Maximum " " " 0.0021 ; 3.9%

* Values published by Andrews, Lynn and Johnston: J. Am. Chem. Soc., 48, 1274 (1926).

A set of values of K derived from cooling curves for Tube 1 is contained in Table IV; another set from heating curves is recorded in Table V. The restriction of data included in the mean value (Tube 2, Table V) occurred because of an obvious discontinuity caused by difference in position of the thermoelement in the specimen. The insulation had worn off the junction of the element, resulting in contact with the platinum capsule at the open end of the re-entrant tube. Since some experiments on phenol and benzophenone were inserted between curves 102 and 107, it was thought advisable to utilize the value of \bar{K} derived from the set of curves immediately preceding and following.

TABLE V

Data on the Apparatus Constant K obtained from Heating Curves

| Substance | Published M. P. °C | *Heat of Fusion cal/mol | Curve No. | Wt. of Specimen (gms.) | Heat of Fusion Area (A) (cm) ² /mol. | K cal/mol ² |
|-----------------------------------------|--------------------------|-------------------------------|--------------|------------------------------|----------------------------------------------------------|-----------------------------|
| Tube 1 | | | | | | |
| Naphthalene | 80 | 4540 | 144 | 0.285 | 819×10^3 | 0.0554 |
| <i>m</i> -dinitrobenzene | 90 | 4150 | 109 | .334 | 764 | .0543 |
| | | | 110 | " | 766 | .0542 |
| | | | 159 | .394 | 805 | .0516 |
| | | | 162 | .390 | 764 | .0543 |
| | | | | | Mean | .0536 |
| <i>m</i> -nitraniline | 112 | 5660 | 125 | .306 | 1045 | .0542 |
| <i>p</i> -nitraniline | 147.5 | 5040 | 152 | .296 | 898 | .0561 |
| | | | 154 | .313 | 972 | .0519 |
| | | | 155 | " | 970 | ** .0520 |
| | | | 156 | " | 942 | .0535 |
| | | | 160 | .303 | 919 | .0548 |
| | | | 161 | " | 934 | .0540 |
| | | | | | Mean | .0537 |
| | | | | | MEAN | .0538 |
| Average deviation from mean 0.0011 ; 2% | | | | | | |
| Maximum " " " 0.0022 ; 4.1% | | | | | | |
| Tube 2 | | | | | | |
| <i>m</i> -dinitrobenzene | 90 | 4150 | 177 | 0.401 | 719 | .0577 |
| | | | 178 | " | 717 | .0571 |
| | | | 179 | .493 | 724 | .0573 |
| | | | 180 | " | 712 | .0583 |
| <i>m</i> -nitraniline | 112 | 5660 | 181 | .197 | 1049 | .0540 |
| | | | 182 | " | 1049 | .0540 |
| | | | 183 | .306 | 1014 | .0558 |
| | | | 184 | " | 1012 | .0559 |
| <i>p</i> -nitraniline | 147.5 | 5040 | 186 | .309 | 866 | .0582 |
| | | | 187 | " | 874 | .0577 |
| | | | 188 | .373 | 828 | .0609 |
| <i>m</i> -dinitrobenzene | 90 | 4150 | 189 | .422 | 672 | .0618 |
| <i>m</i> -nitraniline | 112 | 5660 | 190 | .316 | 923 | .0613 |
| | | | 191 | " | 971 | .0583 |
| | | | 192 | " | 978 | .0579 |

| Substance | Published M. P. °C | *Heat of Fusion cal/mol | Curve No. | Wt. of Specimen (gms.) | Heat of Fusion Area (A) (cm) ² /mol. | K cal/mol ² |
|-----------------------------|--------------------------|-------------------------------|--------------|------------------------------|----------------------------------------------------------|---------------------------|
| <i>m</i> -dinitrobenzene | 90 | 4150 | 197 | .471 | 689 | .0602 |
| | | | 198 | " | 682 | .0608 |
| For Curves 188-198 | | | | | MEAN | .0602 |
| Average deviation from mean | | 0.0012 ; 2% | | | | |
| Maximum | | 0.0023 ; 3.8% | | | | |

* Values of Andrews, Lynn and Johnston: Loc. cit.

** In this experiment, the rate of heating was 5 microvolts per minute.

Application of the Method

In an endeavor to test the apparatus under a variety of conditions, reactions involving the heat of fusion of substances melting near room temperature, that of unstable crystal forms, and the heat of transition of enantiomorphic crystalline solids, were investigated. For reasons discussed above, the heating curve was selected as the suitable method; indeed, in some of the following cases the cooling curve could not have been satisfactorily used.

Heat of Fusion of Phenol and Benzophenone

Some experiments were made with phenol and benzophenone, which melt at 41°C and 48.5°C, respectively, in the attempt to discover the relations between the apparatus constant *K* and the temperature of calorimeter. These substances were chosen because values for their heat of fusion had recently been published by Stratton and Partington,¹ and it was thought probable that these values would be reliable. The apparatus constant derived from this pair of values, however, differed by 17% from Tube 1 and by 14% for Tube 2. In view of this disparity, values for the heat of fusion of phenol and benzophenone were calculated by the use of *K* as derived from Table V, and since, within experimental error *K* does not appear to change with temperature, the values 0.0538 for Tube 1 and 0.0602 for Tube 2 were assumed applicable at the melting temperatures of phenol and benzophenone. The experimental data for the heat of fusion of these substances are given in Table VI and a comparison with the published values is given in Table VII. Although the accuracy of the experimental value for the heat of fusion of benzophenone leaves much to be desired, the evidence appears to indicate that the value published by Stratton and Partington is at least 10% too low.

The phenol used was a colorless Kahlbaum product which, dried over sulfuric acid, showed a satisfactory flat on the heating curve. Because of its hygroscopic nature, it was protected from the air by a cork in the specimen tube and the successive runs were made as rapidly as possible. The benzophenone, from an unknown source, was recrystallized from benzene, and then further purified by partial freezing in a centrifuging tube. When the specimen was about half frozen, the mother liquid was centrifuged off, in a tube

¹ Phil. Mag., 43, 436 (1922).

TABLE VI
Heat of Fusion of Phenol and of Benzophenone
on the basis that
K for Tube 1 = 0.0538;
K for Tube 2 = 0.0602.

| Substance | Tube No. | Curve No. | Wt. of Specimen (gms.) | Heat of Fusion Area (A) (cm) ² /mol | Heat of Fusion (L) cal/mol. |
|--------------|----------|-----------|------------------------|------------------------------------------------|-----------------------------|
| Phenol | 1 | 142 | 0.286 | 501 × 10 ³ | 2700 |
| | | 143 | " | 495 | 2660 |
| | 2 | 193 | .381 | 452 | 2720 |
| | | 194 | " | 444 | 2670 |
| | | | | Mean | 2690 |
| Benzophenone | 1 | 146 | .298 | 873 | 4700 |
| | | 195 | .382 | 761 | 4580 |
| | 2 | 196 | " | 753 | 4530 |
| | | | | | Mean |

TABLE VII
Comparison of Data on the Heat of Fusion of Phenol and of Benzophenone

| Heat of Fusion (L) cal/mol. | Method | Observer | Reference |
|-----------------------------|-----------------------|-----------------------|-----------|
| Phenol | | | |
| 2340 (25°) | Calorimeter | Pettersson & Widman | 1 |
| 2810 | Slope of P-T line | Bridgman | 2 |
| 2730 | Adiabatic Calorimeter | Stratton & Partington | 3 |
| 2690 | Radiation Calorimeter | This investigation | |
| Benzophenone | | | |
| 4310 | Calorimeter | Bruner | 4 |
| 4260 | " | Tammann | 5 |
| 4360 | Slope-of-P-T line | Bridgman | 2 |
| 3950 | Adiabatic Calorimeter | Stratton & Partington | 3 |
| 4600 | Radiation Calorimeter | This investigation | |

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4. *Ber.*, 27, 2102 (1894).
5. *Z. physik. Chem.*, 29, 63 (1899).

of the type described by Skau,¹ the remaining crystals being used. With these as with the other materials, accurate melting point determinations were not made; the form of the time-temperature curves was considered the best indication of the degree of purity of the specimen. Indeed with hygroscopic substances, the increasing concentration of water as impurity could readily be followed on successive heating curves even where special precautions were taken to exclude water vapor.

Heat of Fusion of Chloracetic Acid

Chloracetic acid was chosen as a typical organic compound having unstable crystal forms. It is known to crystallize in three forms—the stable α modification which melts at 61°C., and the labile β and γ forms which melt at 56° and 51° respectively. When the liquid is cooled below 51°C and is allowed to stand quietly, or is inoculated with a crystal of the γ form, the latter crystallizes out. A heating curve of this form can be run in the usual manner. However, if this form is scratched or touched with a crystal of the β form, the crystals transform into this modification; similarly the α form can be obtained either from the liquid or from the β or γ modifications. The data are shown in Table 8; also the data of Pickering,² who measured two definite values for the heat of fusion of chloracetic acid and assumed that, in those cases where more heat had been evolved (on freezing), the α form had crystallized at 61.18°, but made no tests to identify the form present. In the present investigation it was found that in sealed tubes heated above 61° the β or γ forms crystallized spontaneously on cooling, but never the α form.

TABLE VIII

| Heat of Fusion of Monochloracetic Acid on the basis that $K = 0.0538$ for Tube 1 | | | | |
|-------------------------------------------------------------------------------------|-----------------------|-----------------------------------------|-------------------------------------------------|---------------------------|
| Crystalline Form | Curve No. | Wt. of Specimen (gms.) | Heat of Fusion Area (A) (cm) ² /mol. | Heat of Fusion L cal/mol. |
| γ | 132 | 0.262 | 702×10^2 | 3780 |
| | 135 | " | 696 | 3750 |
| α | 133 | 0.262 | 850 | 4570 |
| γ | 149 | .276 | 713 | 3840 |
| β | 150 | " | 828 | 4450 |
| α | 151 | " | 871 | 4680 |
| | | This Investigation Mean Values cal/mol. | | Pickering* cal/mol. |
| | L_α | | 4630 | 3895 |
| | L_β | | 4450 | 3330 |
| | L_γ | | 3790 | — |
| | $L_\alpha - L_\gamma$ | | 840 | — |
| | $L_\beta - L_\gamma$ | | 660 | — |
| | $L_\alpha - L_\beta$ | | 180 | 565 |

* J. Chem. Soc., 67, 664 (1895) Calorimetric Values.

¹ Thesis, Yale University 1925.

² J. Chem. Soc., 67, 664 (1895).

However, the values of Pickering, even if referred to β and γ chloracetic acid, are 12% lower than these found in this investigation.

In order that satisfactory flats might be obtained it was necessary that the Kahlbaum product be purified. Because of its solubility in common solvents, the acid was crystallized in centrifuging tubes from its own liquid. After several fractional crystallizations, the middle fraction was distilled, and the middle portion of the distillate collected. As with phenol the hygroscopic nature of chloracetic acid presented difficulties: to reduce adsorption of water by the specimen, the apparatus was placed over sulfuric acid in a desiccator between runs.

Heats of Transition of Ammonium Nitrate

In order to test the applicability of the apparatus for the evaluation of heat of transition, some transition heats of inorganic salts were measured. Ammonium nitrate exists in five crystalline modifications, their range of stability being shown below.

Polymorphic Forms of Ammonium Nitrate at Atmospheric Pressure

| Form ¹ | Range (Stability) | Transition Temperature ² |
|---------------------|-------------------|-------------------------------------|
| Liquid | 169° to — | |
| Isometric I | 125.2° to 169.6° | 169.6° |
| Tetragonal II | 84.2° to 125.2° | 125.2° |
| Orthorhombic(?) III | 32.1° to 84.2° | 84.2° |
| Orthorhombic IV | -16° to 32.1° | 32.1° |
| Tetragonal V | — to -16° | -16° |

The transitions at 125°C and 84°C proceed readily but the rate of the transition at 32°C proceeds too slowly for this method. The experimental data are given in Table IX and compared with those of previous investigators in Table X. Baker and Adamson's "C.P." ammonium nitrate was used, and since the experiments were preliminary, the substance was not further purified.

Heat of Transition of Mercuric Iodide

In a similar manner the heat of transition of the red form of mercuric iodide to the yellow form at 127°C was measured. The results are shown in Tables IX and X. Merck's mercuric iodide was used without further purification. In this case, as discussed previously, only the heating curve is satisfactory for ready transformation.

¹ Bowen: *J. Phys. Chem.*, **30**, 721 (1926).

² Early and Lowry: *J. Chem. Soc.*, 115, 1387 (1919).

TABLE IX

Heats of Transition of A) Ammonium Nitrate, B) Mercuric Iodide
on the basis that $K = 0.0538$ for Tube 1

| Transition | Curve No. | Wt. of Specimen (gms.) | Heat of Transition Area (cm) ² /mol | Heat of Transition cal/mol. |
|---------------------|-----------|------------------------|------------------------------------------------|-----------------------------|
| a) Ammonium Nitrate | | | | |
| III-II | 115 | 0.304 | 56.6×10^3 | 304 |
| | 119 | " | 58.1 | 315 |
| II-I | 120 | .304 | 182 | 979 |
| | 121 | " | 182 | 979 |
| b) Mercuric Iodide | | | | |
| Red-Yellow | 139 | 1.108 | 119.3 | 642 |

TABLE X

Heats of Transition of Ammonium Nitrate and of Mercuric Iodide

| Heat of Transition cal/mol | Method | Observer | Reference |
|----------------------------|-----------------------|----------------------|-----------|
| Ammonium Nitrate | | | |
| II-I (125.2°C) | | | |
| 950 | Calorimeter | Bellati and Romanese | 1 |
| 1035 | Slope of P-T line | Bridgman | 2 |
| 980 | Radiation calorimeter | This investigation | |
| III-II (84.2°C) | | | |
| 427 | Calorimeter | Bellati and Romanese | 1 |
| 319 | Slope of P-T line | Bridgman | 2 |
| 310 | Radiation calorimeter | This investigation | |
| Mercuric Iodide | | | |
| Red-Yellow (127°C) | | | |
| 3000 | Heat of Solution | Berthelot | 3 |
| 522 | Calorimeter | Schwartz | 4 |
| 695 | Calorimeter | Guinebant | 5 |
| 547 | Slope of P-T line | Bridgman | 6 |
| 640 | Radiation Calorimeter | This investigation | |

References

1. Atti. Ist. Veneto, (6) 4, 1395 (1886).
2. Proc. Am. Acad., 51, 581 (1916).
3. Ann. Chim. Phys., (5) 29, 239 (1883).
4. Z. Kryst., 25, 613 (1896).
5. Compt. rend., 145, 68 (1907).
6. Proc. Am. Acad., 51, 55 (1915).

Conclusion

The advantages of the radiation calorimeter over the ordinary calorimeter procedure may be listed as follows:

1. It is rapid, for if the apparatus is once calibrated, several experiments on a substance can be made and the results calculated in one day.
2. It has a special advantage in the evaluation of certain heats which could otherwise be measured only by a "hot calorimeter" or by an indirect method; for there are a number of transitions—such as the transition of red to yellow mercuric iodide, and ammonium nitrate III to II—which, on heating, are rapid, but on cooling, proceed much less readily and exhibit a marked tendency to undercool. Furthermore, for substances such as chloracetic acid, the form of solid which freezes out is fortuitous, so that, by the usual calorimetric method the sudden chilling of the specimen as it enters the calorimeter may result in either a mixture of crystalline forms or in a form which is not that desired. Indeed, the experience of the authors indicates the possibility that the values of Pickering for the heat of fusion of chloracetic acid (Table VIII) refer to the β and γ forms instead of the α and β forms; for, unless precautions are taken to test the specimen with seed crystals of the several forms, or unless its melting temperature is measured, one cannot be certain as to which form of the solid actually crystallized when the specimen dropped into the calorimeter.

The disadvantages of the apparatus are, in general, associated with those properties of organic compounds—such as poor heat conductivity, instability, etc.—which render difficult calorimetric measurements on them by any method. The open specimen tube precludes the use of a substance which decomposes or oxidizes on heating in air, or which volatilizes appreciably at its transition temperature. One source of error is variation in the position of the thermoelement in the specimen; even with Tube 2 the curve obtained appears to depend to a certain degree on the precise point in the re-entrant tube where contact is made between the thermoelement and the platinum capsule. In the absence of thermal gradients in the specimen the exact position of the thermoelement would be of little importance.

Some variation appears to be due to differences in the precise character of the crystallization of the specimen, differences which became evident when successive time-temperature curves for a specimen, undisturbed between experiments, are compared. Such variation is strikingly indicated in the heating curves (Fig. 4) obtained with a central thermoelement. Not enough evidence was collected to indicate in how far the observed variations are caused by real differences in heat content of the specimen corresponding to incomplete reproducibility of its precise crystal character,* or by differences in aggregation, and consequent change of heat conduction and velocity of transition. For it is to be expected that an alteration in the compactness

* Some evidence has been collected by Griffiths: Proc. Roy. Soc., 89A, 561 (1914), to indicate the specific heat of sodium in the solid state depends on its previous heat treatment—the "annealed" and "quenched" specimens showing a different specific heat.

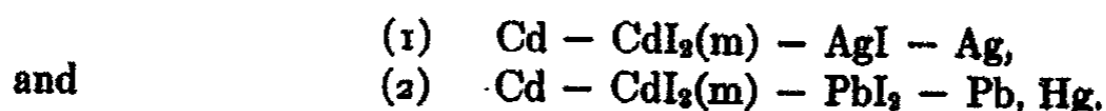
and surface areas of the crystals in the specimen will influence not only the thermal conductivity but also the temperature gradient in the specimen necessary to produce the *flat* in the heating (cooling) curve by the maintenance of the proper rate of transition. Through a study of a metal where the difficulties associated with poor thermal conductivities are at a minimum, and the errors consequently reduced, it may be possible to investigate the precise effect of the nature of crystallization in a specimen on its heat of fusion as measured by a radiation calorimeter.

In spite of such difficulties, and in spite of the small size of the specimen, the maximum deviation from the mean for a series of comparable results is within 5% and it is believed that the mean value for the unknown heat of an organic compound is well within this maximum error.

A STUDY OF THE ACTIVITY OF CADMIUM IODIDE IN AQUEOUS SOLUTION

BY FREDERICK H. GETMAN

In a previous paper¹ we presented the results of an experimental study of the activities of the chloride, bromide and sulphate of cadmium in aqueous solution. The present paper embodies the results of similar studies which have since been made of solutions of cadmium iodide. The experimental procedure has been identical with that followed in the preceding investigation. In the present series of experiments the data has been obtained from measurements of two entirely independent galvanic systems represented by the following schemes:



The latter cell has been shown by Gerke and others² to be reversible to the lead ion.

Materials

(1) *Cadmium Iodide.* Chemically pure cadmium iodide was recrystallized either from conductivity water, or alcohol, before use in preparation of the solutions.

(2) *Silver Iodide.* This salt was prepared from a solution of chemically pure silver nitrate by treatment with pure potassium iodide, care being taken to conduct all operations in a dark room in order to prevent possible reduction of the silver halide by light.

(3) *Lead Iodide.* Lead iodide was prepared by precipitating a solution of chemically pure potassium iodide with a slight excess of chemically pure lead nitrate. The resulting precipitate was washed with distilled water until the wash water was free from nitrate, after which it was allowed to dry at room temperature.

(4) *Hydriodic Acid.* A 50% solution of hydriodic acid, obtained from the Eastman Kodak Company, was redistilled and a solution of the approximate concentration desired was made up by diluting the fraction boiling at 126° to 127°, under 760 mm. pressure, with the estimated amount of conductivity water. The exact concentration was subsequently determined by precipitating a known weight of the solution with silver nitrate and weighing the resulting precipitate of silver iodide.

(5) *Lead.* Stick lead obtained from two different, reliable sources, and guaranteed to be free from silver and other metals, was used in preparing all of the amalgams.

¹ Getman: J. Phys. Chem., 32, 91 (1928).

² Gerke: J. Am. Chem. Soc., 44, 1701 (1922); Taylor: 38, 2295 (1916); Taylor and Perrott: 43, 489 (1921).

(6) *Silver.* The silver employed in the preparation of the silver electrodes was obtained by electrolyzing a solution of pure silver nitrate between an anode of pure silver and a cathode of sheet platinum. The resulting crystals of electrolytic silver were first washed with distilled water, then with a solution of ammonium hydroxide and finally with conductivity water, after which they were rapidly dried in a current of dry, warm air.

(7) *Mercury.* All of the mercury used was exceptionally pure, having been furnished through the courtesy of the Eppley Laboratories.

(8) *Solutions.* All solutions were made up by direct weighing of both solute and solvent, except in the case of solutions of hydriodic acid, where, as pointed out above, the concentration was determined gravimetrically. All concentrations are expressed in mols of solute per 1000 grams of solvent. Conductivity water having an average specific conductivity of 2×10^{-6} mols at 25° was used in the preparation of the solutions.

Experimental Data

In Table I is given the measured values of the electromotive force of cells set up according to the scheme

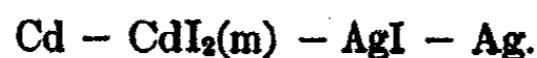
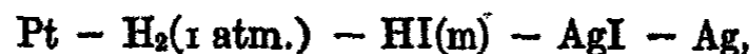


TABLE I

| Conc. (m) (Mols per 1000 gm. H ₂ O) | E.M.F. (25°) volts | Conc. (m) (Mols per 1000 gm. H ₂ O) | E.M.F. (25°) volts |
|------------------------------------------------------|-----------------------|------------------------------------------------------|-----------------------|
| 1.0274 | 0.37402 | 0.0389 | 0.42500 |
| 0.4883 | 0.38688 | 0.0197 | 0.43250 |
| 0.2021 | 0.39926 | 0.0098 | 0.44250 |
| 0.0969 | 0.41024 | 0.0039 | 0.46475 |

The data of the foregoing table are represented graphically in Fig. 1. The tendency of the electromotive force to fall off more and more rapidly with time as the concentration of the electrolyte is diminished was found to be even more marked in the case of the iodide than with the chloride and bromide of cadmium. In fact it was almost impossible to secure satisfactory results with cells in which the concentration of the cadmium salt was much below 0.005 molal. This instability is probably due to several causes, among which increasing solubility of the depolarizer with dilution of the electrolyte is considered to be significant.

In order to compute the activity coefficients of solutions of cadmium iodide from the foregoing data it is necessary to know the potential of the silver-silver iodide electrode in terms of the hydrogen electrode. This has been determined by Noyes and Free¹, as well as by Gerke² and Pearce and Fortsch³. From measurements of the electromotive force of the cell



¹ Noyes and Free: *J. Am. Chem. Soc.*, 42, 476 (1920).

² Gerke: *J. Am. Chem. Soc.*, 44, 1684 (1922).

³ Pearce and Fortsch: *J. Am. Chem. Soc.*, 45, 2852 (1923).

the following values of the electrode potential were obtained: 0.1522 volt (Noyes and Free), 0.1501 volt (Gerke), and 0.1513 volt (Pearce and Fortsch). The mean of these three values, 0.1512 volt, has been taken as the basis of our calculations.

On the assumption that cadmium iodide in aqueous solution behaves as a bi-univalent electrolyte its activity coefficients can be computed by means of the familiar formula,

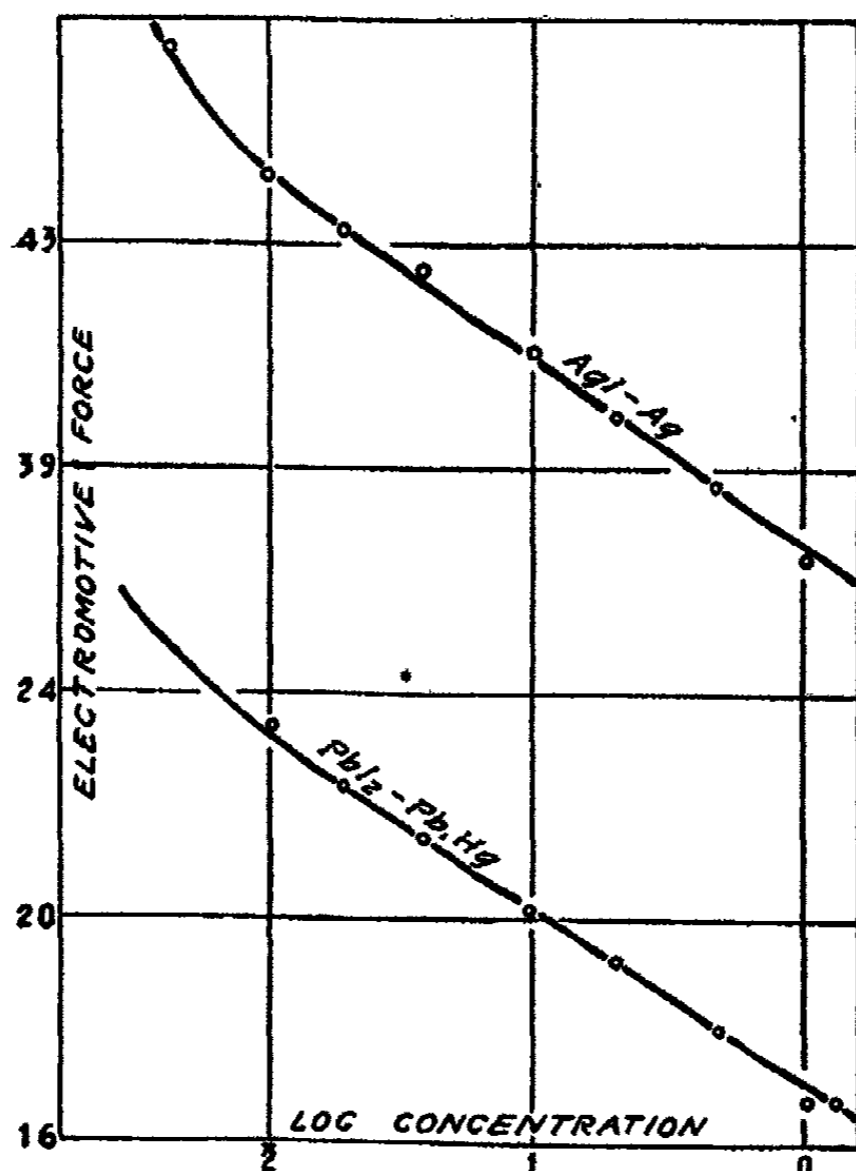


FIG. 1

$$E = E^{\circ} - \frac{RT}{nF} \ln(4m^2\gamma^2).$$

Putting $E^{\circ} = 0.3976$ volt, the value of the electrode potential as determined by Horsch¹, and passing to common logarithms, we have

$$E = 0.3976 - 0.08873 \log (1.588 m\gamma).$$

In Table II will be found the values of γ , computed by substituting in the foregoing equation the successive values of the electromotive force, E , derived from the smoothed values of the electromotive force, E' , as read from the curve in Fig. 1 and referred to the hydrogen electrode.

¹ Horsch: J. Am. Chem. Soc., 41, 1787 (1919).

TABLE II
Activity Coefficients of Solutions of Cadmium Iodide

| m | E' | E | γ | α |
|-------|--------|--------|----------|----------|
| 1.0 | 0.3765 | 0.5277 | 0.022 | — |
| 0.5 | 0.3865 | 0.5377 | 0.033 | 0.16 |
| 0.2 | 0.3995 | 0.5507 | 0.059 | 0.19 |
| 0.1 | 0.4095 | 0.5607 | 0.091 | 0.23 |
| 0.05 | 0.4193 | 0.5704 | 0.14 | 0.30 |
| 0.02 | 0.4325 | 0.5837 | 0.25 | 0.43 |
| 0.01 | 0.4425 | 0.5937 | 0.39 | 0.53 |
| 0.005 | 0.4580 | 0.6092 | 0.52 | 0.63 |

In the fifth column of the table, the corresponding values of the conductivity ratio, α , at 25°, are given for comparison with γ . These ratios were read from a curve plotted from the conductivity data of Jones¹.

The results of a similar series of measurements of the electromotive force of cells set up according to the scheme



are given in Table III.

| TABLE III | | | |
|---------------------------------------------------|----------------------|---------------------------------------------------|----------------------|
| Conc. (m) (Mols per 1000 gm. H ₂ O) | E.M.F. (E') volts | Conc. (m) (Mols per 1000 gm. H ₂ O) | E.M.F. (E') volts |
| 1.2967 | 0.16777 | 0.0196 | 0.22321 |
| 1.0274 | 0.16738 | 0.0099 | 0.23316 |
| 0.4897 | 0.18069 | 0.0050 | 0.24632 |
| 0.2030 | 0.19227 | 0.0040 | 0.24869 |
| 0.0968 | 0.20165 | 0.0030 | 0.25423 |
| 0.0389 | 0.21419 | | |

The potential of the Pb(Hg), PbI₂, I⁻ electrode was computed from the electromotive force of the cell



as recorded in Table IV.

| TABLE IV | | | |
|----------------------------------------------------------------------|--------|--------|----------------|
| Electromotive Force of the Cell | | | |
| Pt—H ₂ (1 atm.) — HI(0.0891M) — PbI ₂ — Pb, Hg | | | |
| E.M.F. (obs.) | Barom. | E | E.M.F. (corr.) |
| 0.22530 | 745.0 | 0.0003 | 0.2256 |
| 0.22458 | 746.8 | 0.0002 | 0.2248 |
| 0.22435 | 748.0 | 0.0002 | 0.2246 |
| 0.22512 | 749.1 | 0.0002 | 0.2253 |
| 0.22555 | 749.8 | 0.0002 | 0.2258 |
| 0.22497 | 750.0 | 0.0002 | 0.2252 |
| | | | Mean 0.2252 |

¹ H. C. Jones: Carnegie Institution Publication, No. 170, p. 49.

The observed values of the electromotive force were corrected for deviations from normal barometric pressure by means of the formula,

$$E = 0.0296 \log 760/p,$$

where p is the observed barometric pressure.

By interpolation in the table of activity coefficients of hydrochloric acid at 25°, as compiled by Lewis and Randall¹, the value of γ for 0.0891 molal acid is found to be 0.823. On the justifiable assumption that the activity coefficients of hydrochloric and hydriodic acids are equal at corresponding dilutions we let $\gamma = 0.823$. Substituting the mean value of the electromotive force, as given in Table IV, in the familiar equation for normal electrode potential,

$$E = E^\circ + 0.1183 \log (m\gamma),$$

$$\text{we have } 0.2252 = E^\circ + 0.1183 \log (0.0891 \times 0.823),$$

$$\text{or } E^\circ = 0.3594 \text{ volt.}$$

The estimated value of this electrode potential given by Gerke² is 0.3579 volt. Accepting the value 0.3594, as here determined, we calculate the values of the activity coefficients given in Table V.

TABLE V
Activity Coefficients of Solutions of Cadmium Iodide

| m | E' | E | γ |
|-------|--------|--------|----------|
| 1.3 | 0.1677 | 0.5271 | 0.017 |
| 1.0 | 0.1715 | 0.5309 | 0.020 |
| 0.5 | 0.1800 | 0.5394 | 0.031 |
| 0.2 | 0.1923 | 0.5517 | 0.058 |
| 0.1 | 0.2010 | 0.5604 | 0.092 |
| 0.05 | 0.2105 | 0.5699 | 0.14 |
| 0.02 | 0.2230 | 0.5824 | 0.26 |
| 0.01 | 0.2335 | 0.5929 | 0.40 |
| 0.005 | 0.2470 | 0.6064 | 0.56 |

It will then be seen that the values of γ calculated from the measured electromotive forces of the two different cells are in close agreement. The mean values of γ given in Tables II and V are plotted against the logarithms of the corresponding concentrations in Fig. 2. Similar curves for the chloride and bromide of cadmium, as given in our preceding paper, together with the curve of conductance ratios for cadmium iodide, are also plotted in Fig. 2.

Discussion of Results

The manner in which the activity coefficients of solutions of cadmium iodide vary with concentration resembles that of the chloride and bromide. As was pointed out in our previous paper, the values of the activity coeffi-

¹ Lewis and Randall: "Thermodynamics," p. 362.

² Gerke: loc. cit., and Chemical Reviews, 1, 384 (1925).

icients of the individual cadmium halides in aqueous solution differ from each other much more widely than do the corresponding values of γ for the halides of the alkali metals.

When the conductivity ratios of solutions of cadmium iodide are plotted against the logarithms of their respective concentrations, we find a much greater divergence from the corresponding curve of activity coefficients than with solutions of either the chloride or bromide.

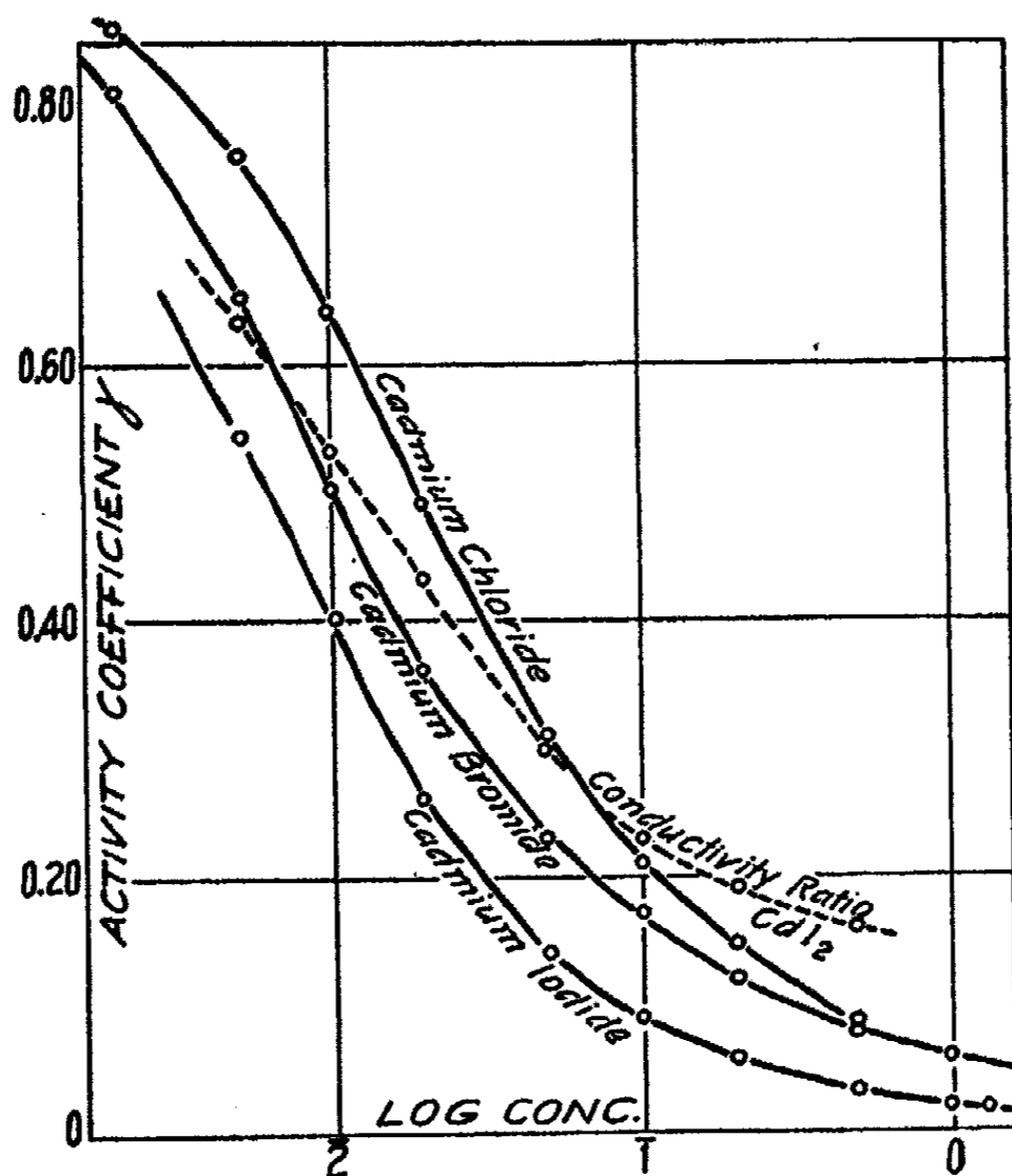


FIG. 2

No trustworthy freezing point data for cadmium iodide being available it has not been possible to compare the values of γ derived from cryoscopic data with those computed from electromotive force measurements. It is hoped, however, that experiments now in progress in this laboratory may soon supply the data necessary for making this interesting comparison.

Summary

(1) The following cells have been studied:

- (1) $\text{Cd} - \text{CdI}_2(m) - \text{AgI} - \text{Ag}$,
- (2) $\text{Cd} - \text{CdI}_2(m) - \text{PbI}_2 - \text{Pb, Hg}$,
- (3) $\text{Pt-H}_2(1 \text{ atm.}) - \text{HI}(m) - \text{PbI}_2 - \text{Pb, Hg}$.

(2) From the measured values of the electromotive force of these cells, at 25°, the values of the activity coefficients, γ , of solutions of cadmium iodide down to 0.005 molal have been calculated.

(3) The values of γ derived from a series of measurements of each of the two cells designated as (1) and (2) were found to be in close agreement.

(4) The activity coefficients of the cadmium halides in aqueous solution differ from each other, forming a progressive series in which the values of γ for the bromide occupy a position approximately midway between those of the chloride and iodide.

*Hillside Laboratory,
Stamford, Conn.*

NEW BOOKS

Colloid Symposium Monograph. By Harry B. Weiser, Editor. 29 × 16 cm; pp. 394. New York: Chemical Catalog Company, 1928. Price: \$6.50. The fifth colloid symposium monograph contains twenty-four papers: Unity in the Theory of Colloids, by H. R. Kruyt; The Stability of Emulsions, Monomolecular and Polymolecular Films—Thickness of the Water Film on Salt Solutions and the Spreading of Liquids, by W. D. Harkins; Adsorption and Crystal Form, by C. H. Saylor; Adsorption from Solution by Ash-free Adsorbent Charcoal, by E. J. Miller; Some Unsolved Problems in the Molecular-Kinetic Behavior of Colloidal Suspensions, by E. O. Kraemer; The Measurement of Surface Tension, Solid against Liquid, by F. E. Bartell and H. J. Osterhof; Investigations on Molecular Sieve Membranes, by Leonor Michaelis; Synthetic Kidneys, by W. D. Bancroft and R. L. Nugent; The Chemistry of Body Processes—the Nature of the Action between Gelatin and Electrolytes, by A. L. Ferguson; Physico-chemical Studies on Protein. III, by R. A. Gortner, W. F. Hoffman and W. B. Sinclair; Relation of Hydrophilic Colloids to Winter Hardness in Insects, by William Robinson; Colloid Types, by E. C. Bingham; The Consistency of Casein Glue, by F. L. Browne and Don Brouse; Plasticity and Solvation of Cellulose Esters, by S. E. Sheppard, E. K. Carver and R. C. Houck; A New Rapid Extrusive Type of Plastometer, by P. M. Giesey and S. Arzooonian; The Falling Sphere Viscometer and Plasticity Measurements, by H. E. Phipps; The Falling Ball Method for the Measurement of Apparent Viscosity of Nitrocellulose Solutions, by J. K. Speicher and G. H. Pfeiffer; The Cellulose Nitrates, by James Craik; The Influence of a Second Liquid upon the Formation of Soap Gels, by H. N. Holmes and R. N. Maxson; Colloids in the Electrodeposition of Metals, by William Blum; Colloidal Ferric Hydrate in Molding Sand, by G. C. Brown and C. C. DeWitt; Hydrated Portland Cement as a Colloid, by A. H. White; Effect of Electrolytes on Electroendosmose through Wood Membranes, by A. J. Stamm; The Physical Chemistry of Color Lake Formation, by H. B. Weiser and E. E. Porter.

Kruyt says that "investigations carried out in my laboratory during the last eight years (the greater part of which has until now been published only in Dutch) have taught that it is no longer necessary to admit this dualism in colloid chemistry. On the contrary, we have stated the following facts: lyophilic sols are polymolecular; their electric charge is of exactly the same type as that of suspensoids; electric charge is as much a stability factor with lyophilic as with lyophobic sols, only we meet with the difference that in the latter case it is the only stability factor, while in the former, the well-known hydration of the lyophilic particles plays a part of equal importance. Finally, we have stated that the importance of hydrogen-ion concentration has been very much exaggerated," p. 11. His conclusions are perfectly true; but one would never guess from this or any other paragraph, that all this had been common knowledge in the United States for many years.

"There is still one point left to be discussed here. We have already said that our point of view must enable us to understand not only the stability conditions, but also the way in which matter gets into colloidal division. We shall not discuss so-called condensation methods, but only dispersion, i.e., those cases in which we start from the solid mass and bring it into colloidal solution.

"Here we meet with a puzzling problem: we have said already that we do not get a gold sol when we shake a piece of gold with water, nor if we boil it; but when we heat starch or gelatin with water, we do get a sol. However, this has nothing to do with the difference between lyophilic and lyophobic sols, for boiling a stone pebble does not give the (lyophilic) silicic acid sols. We can understand the problem if we pay attention to a transition case such as stannic acid. We see once more that a crystal of tinstone cannot be brought into colloidal solution, but the various forms of stannic acid (alpha-, beta- and meta-stannic acids) give sols, each very different, depending on the method of preparing stannic acid and the subsequent treatment. Mecklenburg pointed out that the main question was, how the

particles were in the solid mass that is to be peptized; he and Zsigmondy developed this trend of thought and called attention to the fact that the colloidal particles are formed in the solid material. When this is one large crystal, no peptization is possible. When the primary particles are all free 'protons,' then we get a highly disperse sol; when they stick together as 'polyons,' there will be the unities in the sol, which will therefore be coarse.

"So a necessary condition for dispersing is the performance of particles of colloidal dimensions, not reciprocally bound by fields of force, which are more or less homogeneously distributed (like the cells in a crystal), but bound at distinct points so loosely that they can be easily split up. By what forces? By the effect of a wedge, driven in either by an electric repulsion, consequent upon an electric charge brought about the surface of the two particles or by water molecules attracted by these. Suspensoid peptization has always the former character (SnO₂ with KOH, HgS with H₂S, etc.) emulsoid sol-building, mostly the second. However, we must make the assumption that these primary particles are already formed, say in gelatin, agar, albumen, etc.," p. 17

One wonders whether Kruyt has not over-stated the matter. Are we quite certain that one must have 'protons' in the condensed system? Peptization will take place much easier if that is the case and it is often a necessary prerequisite; but the reviewer does not feel absolutely certain that water would not peptize tannin even if somebody succeeded in making a large crystal of tannin.

Harkins finds, p. 24, that di- β -naphthylamine and symmetrical di- β -triphenyl ethyl urea gives polymolecular films on water which may reach a thickness of 11-40 μ . The other extreme has also been reached, p. 31. "However, with soap as an emulsifying agent a highly concentrated emulsion may be obtained by the formation of a *highly dilute monomolecular film*. The film will produce such an emulsion even if it contains only about one-fifth or one-tenth the number of molecules contained in a tightly packed monomolecular film of the soap. Such an emulsion is not stable, and a process occurs in which the distribution of sizes changes in such a way that the mean drop size increases. This causes a decrease in area per molecule until this area becomes about that to be expected for an ordinary tightly packed monomolecular film."

"The nature of the water film between an aqueous salt solution and an organic phase is of interest in biology. Unfortunately the only information in the literature which has attracted attention indicates that at such an interface salts are positively adsorbed. That this is not true for sodium chloride at the interface between water and benzene is shown by earlier work in this laboratory. The preliminary data obtained in the present investigation show, just as was to be expected, that sodium chloride is negatively adsorbed at such an interface, and that with more concentrated solutions the thickness of the water film is almost exactly the same between salt solution and benzene as it is between salt solution and vapor. With dilute solutions, however, the film is slightly thicker with the former than with the latter system," p. 39.

Saylor has studied the general problem of the crystallization of sodium chloride in octahedra on addition of urea, etc. It is essentially a question of reaction velocity and not of equilibrium, p. 49.

Miller finds that ash-free charcoals adsorb acids and not bases from aqueous solution and that these charcoals therefore cause the hydrolysis of salts like sodium chloride, the unadsorbed liquid becoming alkaline, p. 60.

"Still another fact in striking agreement with the Gibbs adsorption theorem is the negative adsorption of the strong inorganic bases by ash-free charcoal. Theoretically, those substances which raise the surface tension with increasing concentration should be negatively adsorbed. The strong inorganic bases do raise the surface tension and they are negatively adsorbed. Furthermore, in the hydrolytic adsorption of salts the charcoal manifests a selectivity of adsorption of those products of the hydrolysis of salts which lower surface tension and rejects those that raise the surface tension. That is, the acid resulting from hydrolysis is adsorbed and the base is set free," p. 68.

It is a question whether Miller and others do not take too narrow a view of the Gibbs theorem. It is perfectly true that there is a decreased tendency to adsorption if a substance

does not go into the surface film of the solution; but may not the really important factor be the lowering of the hypothetical surface tension of the solid charcoal?

Kraemer devotes thirty-two pages to the conflict between Perrin on the one hand and Burton and Porter on the other. Five pages would apparently have been ample. "These considerations lead to the conclusion that the questions concerning the limits of validity of the ideal kinetic equations as a description of the behavior of colloidal suspensions remain unanswered by the recent studies of sedimentation. The problem of stability of such suspensions has the same status. It has not yet been proven that the forces which prevent collision and adherence of the particles also give rise to the more or less uniform concentration commonly observed in these systems, even when dilute. If these stabilizing forces were to operate with such long ranges as to prevent sedimentation under the influence of gravity, there is every reason to believe that the same forces would likewise reveal themselves in such phenomena as Brownian motion, diffusion, spontaneous fluctuations, as well as sedimentation. Until these various phenomena yield the same conclusions concerning the non-ideality in the kinetic behaviour of suspensions, isolated cases of discrepancy between observations and theory may be suspected to be due to spurious effects of an external character," p. 111.

Bartell says that "there is no controversy over the statement that glass is wetted by water; there does, however, appear to be a difference of opinion as to the correctness of the statement that glass is wetted by mercury. Further thought along this line will make it evident that the commonly used terms, such as "wet," "wettability," "wetting power," etc., are general terms which, up to the present time, have been but poorly defined.

"Consider that one has two different solid substances completely in contact with, or entirely covered by a liquid. In what terms or units shall we compare the relative wettability of the solids or further, in what terms shall we compare the "wetting power" of different liquids for a given solid?

"We shall accept the view that *various solids* are wetted to different degrees by a given liquid; also that a *given solid* may be wetted to different degrees by various liquids. We believe further that the wetting power of each of the various liquids is specific in relation to a given solid. Unfortunately, there are no tables available in the literature which will give even the *relative wettability* of a solid by different liquids. . . .

"It is now quite generally appreciated that "wetting power" is a function not only of the surface tension of a liquid, but also of the *specific attractions* operative between the solid and liquid. An indication of the magnitude of this attraction or force of adhesion solid-liquid can be obtained in case the contact angle solid-liquid is known," p. 113.

"It has been definitely shown that water forms a zero angle of contact with glass. In those cases in which there exists a zero contact angle between solid and liquid, the solid will tend to become wetted spontaneously and completely by the liquid in contact with it. It follows from the well known principles of capillarity that the surface tension of the solid-air system must then be greater than the sum of the surface tension of the liquid and the interfacial tension of the solid-liquid system; i.e.,

$$S_1 > S_2 + S_{12}$$

"At the other extreme it is likewise perfectly evident that no wetting of solid by liquid will occur in case the contact angle is 180° . Surfaces of such materials will come together with no decrease of free surface energy, i.e.,

$$S_1 + S_2 = S_{12}$$

"In those cases in which contact of liquid with solid results in a decrease of free energy there must be the following relationship:

$$S_1 + S_2 > S_{12} \text{ or } S_1 + S_2 = S_{12} + \Delta F,$$

where ΔF represents the decrease in free surface energy. The contact angle, therefore, must be less than 180° . It is obvious that in such cases, adhesion will occur, since ΔF or the work of adhesion is positive. Strictly speaking, then, the solid will become wetted by the liquid. Mercury and glass give a contact angle of about 130° . Since this is less than 180° mercury will, in reality, wet glass.

"When the solid-liquid contact angle is equal to 90° , the force of adhesion may be shown to be equal to one-half the force of cohesion of the liquid molecules for each other. When the contact angle is between 90° and 180° , the force of adhesion solid-liquid is less than one-half the force of cohesion liquid-liquid and a drop of liquid placed on a solid will pull itself together and recede from the solid until its characteristic contact angle is reached. Nevertheless, wetting, according to our views, actually does occur to a certain definite extent. If the solid be forcibly inserted into the liquid we may say that the solid is now wetted by the liquid to a certain definite degree, the degree being dependent upon the magnitude of the decrease in free surface energy.

"When the solid-liquid contact angle is between 0° and 90° , the force of adhesion solid-liquid is greater than one half the force of cohesion liquid-liquid, and such a liquid when placed on the solid will tend to spread upon its surface. In all such cases the extent of spreading will be limited by the surface tension of the liquid and by the contact angle, which is characteristic of this system. In the case of a solid-liquid system which gives a zero contact angle the force of adhesion must then be equal to, or greater than the force of cohesion liquid-liquid.

"The adhesion tension is thus the numerical difference in dynes per cm. or ergs per sq. cm. between the surface tension of the solid against air and its interfacial tension against the liquid. It may be defined as the decrease in free surface energy which occurs when a unit interface solid-liquid is substituted for unit interface solid-air. It is accordingly the energy factor upon whose magnitude depends the wetting or non-wetting of a liquid for a solid surface," p. 116.

"On the assumption that the internal pressure of a liquid is proportional to a function of its surface tension we may calculate from the values obtained for adhesion tensions solid-liquid an approximate value for the pressure of adsorption of a liquid on the surface of a solid. The ratio between the pressure of adsorption of a liquid on a solid and the cohesion pressure of the liquid is then the same as that between the work of adhesion, W_a , and the work of cohesion W_c . If the internal pressure of the liquid is known, the adsorption pressure solid-liquid is given by the product $W_a/W_c \times$ internal pressure. The values obtained in this way will undoubtedly be quite as accurate as those existing in the literature for the internal pressures of liquids. . . .

"These values are such that it appears that the adhesional pressure between carbon and water is at least 1000 atmospheres less than the internal pressure of water, while even in the case of the most strongly adsorbed organic liquids, the excess of adhesional pressure above the internal pressures of the liquids is not more than 3000 atmospheres," p. 132.

"The work to date on adhesion tension (which includes considerable data not contained herein) further confirms the conclusions from the work on adsorption. Those compounds which have a structure favorable to high adsorption likewise show high adhesion tension values. It appears that in the case of a polar hydrocarbon substance the molecular orientation is such that the more polar group extends towards the liquid phase. This appears to hold true for orientation at both carbon and air interfaces.

"In the case of silica as adsorbent, the situation is different. When a liquid is brought in contact with silica the molecule appears to be so oriented that the more polar group is in contact with the silica. Accordingly, those liquids which give with carbon a high adhesion tension give with silica a low adhesion tension. In case of a polar liquid bounded by silica and air, as would be the situation for such a liquid in a capillary tube, it may be considered that at the air interface the polar ends of the molecules would be directed inward toward the liquid, while at the silica interface the polar ends would be directed outward toward the silica," p. 133.

Michaelis says that "the effect of a pure sieve membrane depends largely on the size of the holes. Schematizing a little we may distinguish the following types of sieve membranes: (1) sieve membranes such as filter paper which are impermeable only for large particles; (2) cell filters, e.g., the finest sorts of filter paper which are not permeable for blood corpuscles but are for bacteria; (3) bacterial filters such as clay or kieselguhr filters which are impermeable for bacteria but permeable for colloids in general; (4) colloid filters

which are permeable for the so-called truly dissolved substances but impermeable for colloids. These are membranes of parchment paper, animal skins, etc., and the usually used collodion membranes. Finally there are molecular sieve membranes which exert an influence even on the diffusion of kinds of molecules of decidedly non-colloidal character, such as sugar, urea, and simple salts. Among these membranes is the best known one, the copper ferrocyanide membrane of W. Traube, which played a great rôle in the development of the theory of osmotic pressure. The disadvantage of this membrane is that it is very delicate and mechanically little resistant even when imbedded in the frame-work of a clay cell. In order to operate with these membrane-forming substances, copper sulfate and potassium ferrocyanide, must be present on either side of the membrane. This condition renders detailed investigations very complicated," p. 135.

The actual experiments were done with a dried collodion membrane; but no proof is given that this is a sieve membrane. Michaelis believes that the speed of diffusion depends on the molecular size or even better on the molecular volume, p. 139; but the reviewer is very sceptical as to the accuracy of this conclusion. It is probable that the results would have been quite different if acetone had been taken as one of the solutes.

Bancroft and Nugent show, p. 149, that the problem of anomalous endosmose must be worked out in some detail before one can hope to make any real progress with the question of how the kidney functions.

Ferguson is one of the irreconcilables. "The topic which I wish to consider in this introduction, however, is not particularly this somewhat unsatisfactory condition of colloid chemical literature, but the general attitude assumed by many investigators of colloid phenomena in their approach to the subject. The indications point strongly toward a deliberate attempt to build a kind of Chinese wall around what they choose to call the field of colloid chemistry. Much energy has been and is being spent to demonstrate that in this field of colloidal chemistry new forces of some mysterious nature are at work. The impression is given that one who enters must leave behind him all the working tools of classical chemistry and be prepared to develop new methods of attack and to interpret his data in terms of new principles and a new language, and develop a set of new theories and generalizations. In this new field one should not talk about solutions and the great mass of laws, principles, and theories developed in connection with them; one must not mention chemical reactions and the quantitative relations which they imply; chemical forces and chemical energy must be displaced by surface tension and adsorption or some other even less understood concepts; the term atoms, molecules, chemical compounds and solute must be dropped from the vocabulary of one who would be a colloid chemist, and in their places must be substituted such terms as adsorption complex, micelle, dispersed phase, etc.

"This attempt at isolation and segregation of so-called colloid phenomena from classical chemistry is, in my judgment, fundamentally unscientific and unwarranted by facts. It is unscientific because the outstanding objects of science are simplification, coordination, unification, the expression of facts and information in terms of well known and well established laws, formulas, generalizations and theories. Even the colloid chemists who are attempting to build this wall admit that a large portion of the phenomena in colloid chemistry may be satisfactorily explained on the basis of the principles of classical chemistry, but since these phenomena may be explained also in terms of their own newly developed language, they choose the latter. In so doing they adopt the attitude of the secessionist. Instead of working for unity and harmony and simplicity, they are developing dissension, segregation and disunion," p. 159.

The reviewer questions the accuracy of the statement, p. 162, that Bechhold succeeded with his ultra-filter in filtering out anything which everybody admitted was in true solution.

Gortner treated different wheat flours with normal solutions of various salts and obtained the following values, p. 187, for the average percentage peptization of protein: KF, 13.1; KCl, 22.8; KBr, 37.2; KI, 63.9. This is a rather remarkable case of the Hofmeister series, not due, as Loeb assumed, to the pH of the solution. This raises the question as to what a globulin is and how one knows it, p. 192.

"Just why certain workers should accept the viewpoint that aqueous systems of starches, cellulose, rubber, and other lyophilic and lyophobic systems may react as colloids but that proteins are characterized by an entirely different behavior is incomprehensible. However, even Loeb's data are capable of more than one interpretation, as is indicated by the cited comments of Rinde and Hill, and the fact that a lyotropic series exists, which Loeb admits would not be explainable by his theory, makes it essential that we use all of the tools of research which we possess, in our study of protein systems. We know that the protein molecule is large enough to bring the size of the particles well within the boundary of the colloid realm. We believe that, with the exception of the albumins, most proteins exist in 'solution' as micelles. If there are electrokinetic forces at interfaces between water and starch, cellulose, or glass, there must be electrokinetic forces at the interfaces of a protein-water system and to ignore such forces is only to delay a full and complete understanding of protein behavior."

Robinson experimented with a hardy, a neutral, and a non-hardy species of insect and found, p. 218, that "the different species gained or lost in bound water in direct proportion to the winter hardiness."

There are either some very bad misprints in Bingham's article or else he has not said what he meant to say. "It appears possible that nitrocellulose and butyl acetate are miscible in all proportions. Nitrocellulose and toluene seem to be mutually insoluble. Very small percentages of nitrocellulose are sufficient to render butyl acetate and toluene immiscible," p. 226. This is undoubtedly a typographical error; but the reviewer has been quite unable to make out what the next paragraph really means. "Moore has shown that in 100 grams of solvent mixture, the concentration of butyl acetate, necessary for complete solution, is nearly independent of the weight of the sample of nitrocellulose, as shown in Fig. 6. The results may be expressed in another way by stating that the weight of nitrocellulose dissolved in 100 grams of the solvent is directly proportional to the weight of the sample," p. 228. This sounds quite impossible if the nitrocellulose is homogeneous.

Browne says that "consistency studies of casein glue are significant to the woodworker in two connections. In the first place, since the fundamental principle underlying the production of strong joints in gluing wood, given a suitable woodworking glue, is the reciprocal relationship between pressure and glue consistency at the time of applying the pressure, the investigation of factors influencing gluing operations can often be resolved into a laboratory measurement of their effect on consistency without resort to the difficult and tedious technic of joint strength tests. In the second place, consistency is a conveniently measurable physical property which is extremely sensitive to changes taking place in the chemical composition or colloidal state of the glue itself. It is believed that a study of the rate of change in the consistency during the working life of casein glues of different kinds will throw much light on the very important but hitherto inadequately studied property of the *permanence* of water-resistant casein glues under prolonged exposure to damp conditions. Glues which are highly water resistant when first prepared do not necessarily remain so after they have been subjected to moisture for some time," p. 230.

Sheppard objects to Byron's explanation of the action of ethyl alcohol as being too specific. "There are many mixtures of liquids which are better solvents for cellulose esters than either of the liquids pure, in which there is no particular evidence of polymerization. It appears that any theory which is to be satisfactory must be general enough to apply to all cases," p. 243. There is here the implied assumption that mixtures of liquids can only act in one way.

Sheppard himself inclines to the polar, non-polar theory of Hildebrand as adapted by Highfield, who assumes, "with very good evidence, that one particular mixture of acetone and water has the optimum polar characteristics for dissolving nitro-cellulose. No matter what the composition of the acetone-water mixture, the nitrocellulose aggregates will tend to absorb a mixture containing this optimum ratio. Therefore, for example, if the acetone alcohol mixture contains less water than the optimum, the nitro-cellulose aggregates will be surrounded by a liquid mixture, differing in composition from that of the bulk of the

solvent, and this will tend to restrict the free flow of the molecules of the liquid. With excessive water, the absorbed solvent will be richer in acetone than the remaining solvent," p. 247. This may or may not be true; but it does not appear from anything in the paper how Sheppard accounts for the action of alcohol on pyroxylin. It is a bit unkind to reject an apparently good explanation on the ground of its being too specific and then not to show how the supposedly general explanation applies.

Phipps shows that the falling sphere viscometer gives a curve which does not coincide with the one obtained with the Bingham and Murray plastometer, p. 206. Its use is limited to the lower portion of a normal plasticity curve. Speicher and Pfeiffer summarize their results as follows, p. 272: "Using the falling ball method, and calculating results by Stokes' Law as modified by Ladenburg, results consistent among themselves were obtained with nitrocellulose solutions. Very low viscosity types of nitrocellulose produce solutions which not only give consistent results by the falling ball method but also show the same relation between the falling ball method and a capillary tube method that castor oil shows. With the higher viscosity nitrocelluloses a change in shearing stress as represented by a change from the falling ball to a capillary tube viscometer gives a relation different from castor oil. The capillary tube instrument used was not a highly enough refined instrument to justify more than comparative measurements; consequently the results cannot be interpreted in terms of absolute values."

Craik finds that the peptizability of cellulose nitrates can be predicted from a knowledge of the nitrogen content of the surfaces of the particles, p. 273; but his results were obtained by denitrating the surface or nitrating it higher. He was not able to start with two different cellulose nitrates and to put them together synthetically, so that one or the other was on the outside.

For some unspecified reason, Holmes tried to disperse potassium stearate in hot turpentine and to secure a gel (meaning a jelly) on cooling; but was unsuccessful except on one occasion when a trace of water was present. The effect of adding water and oleic acid was therefore studied, pp. 287, 296. The data are recorded and no conclusions are drawn.

Blum sums up his paper as follows, p. 312:—"The preceding discussion might almost better have been entitled "Unsolved Problems on the Effects of Colloids in Electrodeposition," as it shows so clearly the inadequacy of existing knowledge as a basis for any comprehensive theory of the subject. The progress in the past five years is, however, far from discouraging. New methods have been applied and old ones have been improved. Qualitative observations have been succeeded by definite quantitative measurements of such important factors as acidity, polarization, and throwing power. The X-ray is being applied to the problem with promising results, which, however, require more extended study for their complete interpretation. The new concepts of physics and physical chemistry have given at least an inkling of what happens at an interface between a metal and solution during electrolysis. It is, therefore, reasonable to expect that within the next ten years this subject of colloids in electrodeposition, which has always been shrouded in an air of mystery and empiricism, will take its rightful place as one of the most important phases of electrochemistry."

It seems to the reviewer that Blum has been unduly despondent and apologetic. With a little more courage he might have written his paper as a paean of rejoicing over things accomplished. The paper would then have been very much more interesting and somewhat more accurate.

DeWitt and Brown point out that "a molding sand has been defined by Littlefield as any material which when moist can be formed into a mold from which usable metal castings may be made. This definition includes all combinations of sand and clay or other material, and it implies all desirable qualities that a molding sand must have, the two most important of which are bonds, so that the mold may have sufficient strength to support the metal while being poured, and permeability to gases, so that the gases may readily escape giving a sound casting free from blow holes," p. 313.

"The strengths of the natural and synthetic molding sands are decreased to almost the same degree by heating to 600°F for three hours. This affords further evidence that the

natural molding sand has been substantially duplicated by synthetic means. The permeabilities of the natural and synthetic sands are increased to about the same degree by the heat treatment. The data presented indicate that the bond, permeability, and durability of high grade natural molding sand can be substantially duplicated by synthetic means using adsorbed ferric hydrogel as a bonding agent. The numerous constituents of natural molding sand identified by Condit are not essential to the properties of molding sand. It has just been shown that the properties of a high-grade molding sand can be duplicated by the use of only three materials, sand, kaolin, and ferric hydrosol," p. 340.

"The presence of the hydrated iron oxide film on the silica is shown to exert a marked influence on the strength of silica-kaolin mixtures. Hydrated iron oxide films on both silica and kaolin give a further increase in strength, especially at the higher water contents.

"The permeability of the silica-kaolin decreases with successive additions of water while the permeability of the silica-kaolin-iron oxide combinations shows an increase with water content. This may be taken as an indication that adsorbed hydrated iron oxide on the particles of silica is present as a gel which takes up water and swells thereby forming larger particles tending to become spherical or causing the separate grains to agglomerate, in either case increasing the permeability of the mass," p. 344.

White's conclusions, p. 359, are that "Portland cement clinker on hydration forms products some of which are crystalline and some of which form a stiff gel. This gel absorbs and gives up water with changing humidity of the air. A bar of neat cement may change in length more than 0.1 per cent with alteration in atmospheric humidity. The linear expansion when changed from dry air to water will be greater than this and may be as great as 0.5 per cent. The gel retains this reversibility at atmospheric temperature for at least twenty years, and there is nothing to indicate that it may not continue indefinitely. The magnitude of the expansion increases with the number of alternations between the dry and the wet state, due to the progressive hydration of particles of unchanged clinker. When a bar of hardened cement is transferred from dry air to benzene, the capillaries become slowly filled with benzene with resultant increase in weight and apparent specific gravity, but without any change in the length of the bar. When the same bar, after evaporation of the benzene, is transferred to water, the capillaries become filled with water with a resultant increase in weight, apparent specific gravity and length. The volume of water adsorbed may be three times as great as that of the benzene absorbed in the prior test. If it be assumed that the benzene filled the larger capillaries and that the surplus volume of water was all adsorbed in the micropores, the increase in volume of the bar should give a measure of the compressed volume of the water. An assumption of this sort indicates that the water was compressed to half its volume, but the figure cannot be given much weight because of the uncertainties as to the amount of air remaining in the capillaries on immersion in benzene and in water respectively. So also the increase in apparent specific gravity cannot be given much weight in computing pressures. Freezing tests on bars of well hardened neat cement saturated with water fail to show any expansion although the bars contain about 11.0 per cent of water of which two-thirds is in such a form that it will evaporate in dry air and be absorbed again on immersion in water. In fact the bars of cement shrink to a greater degree than cast iron as the temperature drops further below the freezing point. This failure to expand at the freezing point may indicate a very high compression of the water or it may indicate that the water was already in the solid state before it was frozen."

Stamm finds, p. 367, that "dilute alkali solutions increase the rate of electroendosmose through wood membranes, and dilute acid solutions decrease it in such a way as to give a straight-line relation between rate and pH. Dilute acids affect the membrane permanently, perhaps causing hydrolysis in the internal surface, in such a way as to reduce the rate of flow. Concentrated acids and bases both reduce the rate of electroendosmose permanently." Weiser and Porter show, p. 386, that Marker and Gordon were wrong in postulating the formation of compounds when Orange II is taken up by alumina. They also show, p. 383, that the experiments by Bull and Adkins in the reviewer's laboratory on the adsorption of sodium alizarate by alumina are apparently wrong. They found no increase of alkalinity

when alumina was treated with a sodium alizarate solution and that practically all the sodium stayed in the solution, being neutralized by chlorine which came out of the alumina gel. Unpublished experiments in the reviewer's laboratory indicate a difference of color for free alizarin taken up by alumina and for sodium or ammonium alizarate taken up by alumina. Until this discrepancy is cleared up, the matter is still a debatable one. It seems to the reviewer that it would be interesting to make some experiments with a really pure alumina, prepared by the action of amalgamated aluminum on distilled water.

Wilder D. Bancroft

The Logic of Modern Physics. By P. W. Bridgman. 32 × 16 cm; pp. xiv + 228. New York: The Macmillan Company, 1927. Price: \$2.50. In the preface the author says: "This excursion into the field of fundamental criticism by one whose activities have hitherto been confined almost entirely to experiment is not evidence of senile decay, as might be cynically assumed. I have always, throughout all my experimental work, felt an imperative need of a better understanding of the foundations of our physical thought and have for a long time made more or less unsystematic attempts to reach such an understanding. Only now, however, has a half sabbatical year given me leisure to attempt a more or less orderly exposition," p. v.

In the introductory chapter we read that "before Einstein, an ever increasing number of experimental facts concerning bodies in rapid motion required increasingly complicated modifications in our naive notions in order to preserve self-consistency, until Einstein showed that everything could be restored again to a wonderful simplicity by a slight change in some of our fundamental concepts. The concepts which were most obviously touched by Einstein were those of space and time, and much of the writing consciously inspired by Einstein has been concerned with these concepts. But that experiment compels a critique of much more than the concepts of space and time is made increasingly evident by all the new facts being discovered in the quantum realm.

"The situation presented to us by these new quantum facts is two-fold. In the first place, all these experiments are concerned with things so small as to be forever beyond the possibility of direct experience, so that we have the problem of translating the evidence of experiment into other language. Thus we observe an emission line in a spectroscope and may infer an electron jumping from one energy level to another in an atom. In the second place, we have the problem of understanding the translated experimental evidence. Now of course every one knows that this problem is making us the greatest difficulty. The experimental facts are so utterly different from those of our ordinary experience that not only do we apparently have to give up generalizations from past experience as broad as the field equations of electrodynamics, for instance, but it is even being questioned whether our ordinary forms of thought are applicable in the new domain; it is often suggested, for example, that the concepts of space and time break down," p. viii.

The four chapters are entitled: broad points of view; other general considerations; detailed consideration of various concepts of physics; special views of nature.

"Hitherto many of the concepts of physics have been defined in terms of their properties. . . . Now there is no assurance whatever that there exists in nature anything with properties like those assumed in the definition, and physics, when reduced to concepts of this character, becomes as purely an abstract science and as far removed from reality as the abstract geometry of the mathematicians, built on postulates. It is a task for experiment to discover whether concepts so defined correspond to anything in nature, and we must always be prepared to find that the concepts correspond to nothing or only partially correspond. In particular, if we examine the definition of absolute time in the light of experiment, we find nothing in nature with such properties.

"The new attitude toward a concept is entirely different. . . . In general, we mean by any concept nothing more than a set of operations; the concept is synonymous with the corresponding set of operations. . . . We must demand that the set of operations equivalent to any concept be a unique set, for otherwise there are possibilities of ambiguity in practical applications which we cannot admit." p. 4.

"There probably is no statement either in Einstein or other writers that the change described above in the use of "concept" has been self-consciously made, but that such is the case is proved, I believe, by an examination of the way concepts are now handled by Einstein and others. For of course the true meaning of a term is to be found by observing what a man does with it, and not by what he says about it. We may show that this is the actual sense in which concept is coming to be used by examining in particular Einstein's treatment of simultaneity," p. 7.

"Another consequence of the operational character of our concepts, almost a corollary of that considered above, is that it is quite possible, nay even disquietingly easy, to invent expressions or to ask questions that are meaningless. It constitutes a great advance in critical attitude toward nature to realize that a great many of the questions that we uncritically ask are without meaning. If a specific question has meaning, it must be possible to find operations by which an answer may be given to it. It will be found in many cases that the operations cannot exist, and the question therefore has no meaning," p. 28.

"To adopt the operational point of view involves much more than a mere restriction of the sense in which we understand "concept," but means a far-reaching change in all our habits of thought, in that we shall no longer permit ourselves to use as tools in our thinking concepts of which we cannot give an adequate account in terms of operations. In some respects thinking becomes simpler, because certain old generalizations and idealizations become incapable of use; for instance, many of the speculations of the early natural philosophers become simply unreadable. In other respects, however, thinking becomes much more difficult, because the operational implications of a concept are often very involved," p. 31.

"I believe many will discover in themselves a longing for mechanical explanation which has all the tenacity of original sin. The discovery of such a desire need not occasion any particular alarm, because it is easy to see how the demand for this sort of explanation has had its origin in the enormous preponderance of the mechanical in our physical experience. But nevertheless, just as the old monks struggled to subdue the flesh, so must the physicist struggle to subdue this sometimes nearly irresistible, but perfectly unjustifiable desire. One of the large purposes of this exposition will be attained if it carries the conviction that this longing is unjustifiable, and is worth making the effort to subdue," p. 47.

"The conviction, arising from experience, that the future is determined by the present and correspondingly the present by the past, is often phrased differently by saying that the present causally determines the future. This is in a certain sense a generalization of the causality concept. It is one of the principal jobs of physics to analyze this complex causal connection into components, representing as far as possible the future state of the system as the sum of independent trains of events by each individual event of the present. How far such an analysis is possible must be decided by experiment. It is certainly possible to a very large extent in most cases, but there seems to be no reason to expect that a complete analysis is always possible," p. 88.

"The concept of energy may be extended from mechanical systems to all systems with which we are acquainted; the operations by which meaning is given to the extended energy concept involve the generalized conservation principle, or the first law of thermodynamics. The extension to thermal systems is immediate; the inclusion of optical and electrical systems in the scheme was a most important physical step, which of course required careful experimental justification. Because of its wide range of application, the energy concept has now come to be regarded as one of the most important in physics; this idea was held by Ostwald twenty and more years ago, and is now much to the front because of the connection between mass and energy indicated by the theory of relativity, and the important rôle assigned to energy levels in spectrum analysis," p. 109.

"Finally, we emphasize a fact already implicitly mentioned, namely, that no physical significance can be directly given to flow of heat, and there are no operations for measuring it. All we can measure are temperature distributions and rates of rise of temperature. As at present defined, a heat current is a pure invention, without physical reality, for any

determined heat flow may always be modified by the addition of a solenoidal vector, with change in no measurable quantity," p. 130.

"There are other interesting questions of a fundamental thermodynamic character, such, for example, as whether the entropy concept has any general significance apart from the scale of our measuring instruments, and that is the operational significance of applying thermodynamic concepts to radiation, but we shall not consider these questions here," p. 131.

"Now we have already seen, in discussing the concepts of mechanics, that the operations by which mechanical mass is defined cannot be carried out at high velocities, so that either the concept of mechanical mass becomes meaningless at high velocities, or we must adopt another definition. In attempting to give this new definition of mass at high velocities, we are driven to a result of special relativity theory, namely that all mass, mechanical or electrical, must be the same function of velocity. If now electrical mass can be found in terms of velocity, our immediate problem is solved and we shall be in a position to complete the experimental check of the equation. But as a matter of fact, in order to determine electrical mass, we have to use that equation which we are now engaged in trying to establish. Logically we have again the vicious circle, the physical significance of which is that independent operations do not exist for giving unique meaning to the concept of force on a charge at high velocity.

"We seemed so close to our goal a minute ago, that we may allow ourselves to jump the logical chasm, and assume that the equation is correct. Electrical mass now becomes a definite function of velocity, mechanical mass the same function, and we are in a position to compare the actual acceleration received by a charge in a field with that calculated by the equation. Our conviction, on the basis of all experience up to the present, is that the two accelerations will be found to agree," p. 138.

"The status of light is exactly the same as that of an electric field; there is not the slightest warrant for ascribing physical reality to either at points of empty space—light and field-at-a-point have no meaning until we go there and make experiments with some material thing. Of course the electromagnetic theory of light makes this resemblance inevitable, provided the theory and our views of the nature of light and the field are correct," p. 153.

"We now ask why it is that Einstein was able in the general theory of relativity to obtain new and physically correct results from general reasoning of an apparently purely mathematical character. We are convinced that purely mathematical reasoning never can yield physical results—that if anything physical comes out of mathematics it must have been put in in another form. Our problem is to find where the physics got into the general theory. There are two questions to be disentangled here: we have to consider in the first place the significance of the fact that Einstein has been able to describe relations in nature of mathematical form, and in the second place of the fact that he was able to arrive at the mathematical formulation of these physical relations by reasoning of apparently a purely mathematical character, from postulates of merely formal mathematical content (invariance of natural laws in generalized coördinates)," p. 169.

"With respect to the second question we may stop to notice that the special theory stands in quite a different position from the general theory. The special theory is much more physical throughout; its postulates are physical in character, and it is obvious that the physics got into the results through the postulates. It seems to me without question that Einstein showed the intuitive insight of a great genius in recognizing that there are mutual relations between physical phenomena which can be described in very much simplified language in terms of concepts slightly modified from those already in common use. In view of the remarks made in the nature of light, it is legitimate to wonder, however, whether the formulations of even the special theory will always stand. It seems to be true that *all* the facts of nature, even in the absence of a gravitational field, cannot be connected by the simple formulations of the special theory; that the physical relations are simple only in a sub-group; and that if we wish to deal with *all* optical phenomena, we have carried our simplifications too far, for the emission of a light signal is not a simple event, and light is not in nature like a thing travelling. Just the sorts of physical thing which are ignored in treating light as the special theory does are coming to be more and more important in the

minds of physicists, and this is a reason for wondering whether ultimately Einstein's special theory may not be regarded as a very convenient way of tying together a large group of important physical phenomena, but not as being by any means a full or complete statement of natural relations," p. 170.

"It is often said that quantum phenomena are inconsistent with ordinary mechanics, and proofs of this assertion are often offered. I believe that no such proof, in the spirit in which the attempt is usually made, can be correct, for it seems to me that the remark of Poincaré applies, namely that any sort of behavior can be imitated by a mechanical system, provided it is only complicated enough," p. 190.

"I believe it meaningless to speak of discontinuous time. We may have phenomena discontinuous in space and time, but not discontinuous space or time," p. 191.

"The invention of new concepts is certainly not an easy thing, and is something which physics has always deliberately, and perhaps justifiably, shirked, as shown by the persistent attempts to carry the notions of mechanics down into the finest structure of things. This shirking has not had bad results, but on the contrary good results, as long as physics has been primarily concerned with phenomena near the range of ordinary experience, but I believe that as we get farther and farther away from ordinary experience, the invention of new concepts will become an increasing necessity," p. 195.

"It seems fairly evident then that the laws of nature cannot be reduced to either those of mechanics or of electricity, nor probably, as is suggested by quantum phenomena, to a combination of both. This of course does not preclude the possibility that the laws still may be simple when expressed in other forms. An example of such a broad general law that goes deeper than mechanics or electrodynamics is probably afforded by the second law of thermodynamics when extended to include radiation phenomena," p. 200.

"In general, we cannot admit for a minute that a statistical method, unless used to smooth out irrelevant details, can ever mark more than a temporary stage in our progress, because the assumption of events taking place according to pure chance constitutes the complete negation of our fundamental assumption of connectivity; such statistical methods always indicate the presence of physical complications which it must be our aim to disentangle eventually," p. 206.

Wilder D. Bancroft

The Constitution of Glass. Edited by W. E. S. Turner. 14 × 22 cm. Sheffield: The Society of Glass Technology, 1927. The volume before us consists of a series of twelve papers all of which have been already published between the years 1925-27. In view of our very imperfect knowledge and inadequate theories respecting the constitution of glass, this collection of papers will serve a very useful purpose by bringing together, in a convenient form, some of the more important results of experimental investigation and the theoretical views regarding the constitution of glass. Being a collection of papers by different authors and of diverse character, the volume, as the editor states, "lacks the systematic presentation which a single author or compiler may have given to it," and its chief value, perhaps, may be looked for in "stimulating additional investigators to enter a field so fascinating and so comparatively virgin."

The twelve papers which form the collection are: the nature and constitution of glass, by W. E. S. Turner; glasses as supercooled liquids, by G. Tammann; on the constitution and density of glass, by A. Q. Tool and E. E. Hill; on the viscosity and allotropy of glass, by H. LeChatelier; the viscosity of glass, by V. H. Stott; the ternary system sodium metasilicate-calcium metasilicate-silica, by G. W. Morey and N. L. Bowen; x-ray diffraction measurements on some soda-lime-silica glasses, by R. W. G. Wyckoff and G. W. Morey; some remarks on the constitution of glass, by F. Eckert; the structure of quartz, by Sir W. H. Bragg; general discussion of the foregoing papers; the viscous properties of glass, by V. H. Stott; the structure and constitution of glass, by W. Rosenhain.

A glance through these different papers which deal with almost every aspect of the problem of the constitution of glass, shows that one is really only at the very beginning of attack on the problem and that opinion is almost as diverse as the number of workers.

One cannot but feel that in many of the investigations, the number of variables is too great to allow of definite conclusions being drawn. Recent investigations on single substances in the vitreous condition seem to indicate that there are certain peculiarities of behaviour which differentiate the vitreous from the liquid and crystalline states, and it seems important to investigate this behaviour more fully. In view of the vagueness which at present invests the problem of the glassy state, the hypothesis put forward by Rossnain that in a glass we are dealing with an assembly of atoms in which inter-atomic linkages tend to be formed in certain definite directions, and that only the number of inter-atomic linkages which are operative may vary, is of interest and may prove of value in directing investigation.

For all who are interested not only in glass but in the vitreous state of matter, the collection of papers included in the volume under review will be of much value, and will be welcomed by them.

Alex. Findlay

The Phase Rule and its Applications. By Alexander Findlay. 21 × 14 cm; pp. xv + 328 London and New York: Longmans, Green and Company, 1927. Price: 10s. 6d. This sixth edition of Professor Findlay's well-known and successful book is dedicated to Wilder D. Bancroft, and the material presented has undergone a thorough revision. Certain parts of the volume, more especially those dealing with equilibrium in one- and two-component systems, have been re-cast and re-arranged. In the reviewer's opinion, considerable improvement has been effected thereby. Room is found for some reference to the problem presented by intensively dried substances, as also for a brief discussion of the Smits theory of allotropy in relation to the phase rule.

An interesting and valuable feature is a new chapter in which the practical applications of equilibrium diagrams, in connexion more particularly with the winning of salts by crystallisation, are discussed and illustrated.

There are but few points on which comment might be offered and these are of minor importance. The reviewer notes that Professor Findlay used the term "instable," although this is a rare or even obsolete word. It may seem illogical to write "unstable" and "instability," but the former of these is firmly established by usage and should be employed.

A slight error appears to have crept into the author's description (p. 114) of the cooling record for certain binary mixtures which deposit a compound with incongruent melting point. A final eutectic arrest will be observed only for those mixtures the composition of which lies between the transition point and the imaginary summit corresponding to the compound,—not, as the author suggests, for all mixtures lying between the transition point and the pure constituent B.

The volume is written with Professor Findlay's usual clearness and competence and will be found indispensable by all students of physical chemistry.

J. C. Philip

Atomic Form with Special Reference to the Configuration of the Carbon Atom. By Edward E. Price. Second edition. 22 × 14 cm; pp. xxi + 223. London and New York: Longmans, Green and Co., 1926. Price: 23.00. In the preface to the second edition the author says that "while the main features of the book are the same, the theoretical structure of graphite and diamond has now been developed in accordance with the theory of atomic form, and chapters have been added on steric hindrance, mellitic acid, and silicon, while other chapters have been enlarged."

The headings of the chapters are: introduction; monovalent and divalent atoms; the carbonoid and ethyloid; benzene and some of its derivatives; the allotropic forms of solid carbon (*a*); law of even numbers; tautomerism; isoprene and rubber; silicon; triphenyl-methane and hexamethyl-ethane; mellitic acid and the carbon molecule; steric hindrance; isomerism and optical activity; changes in the carbon framework; cyclic compounds; condensed rings; concluding observations.

The author admits quite frankly, p. 2, that "if one considers a substance in the gaseous state as consisting of spherical or ellipsoidal forms, it is difficult to conceive of their arran-

ging themselves according to geometric laws, as soon as the temperature has been lowered sufficiently to reduce the movements of the atoms to a certain degree; but if the atoms themselves have definite geometric forms, then arrangement in an orderly crystal structure, so as to produce definite geometric figures peculiar to each atom, appears to be the natural result of the withdrawal of heat."

"We have theories in which all matter is deemed to be entirely electrical, and theories are put forward where the electrons are assumed to be in constant motion. There are other theories which are based upon the view that the protons and electrons are held to be in a static condition. Further there are systems in which the revolutions of the electrons are assumed to adopt orbits both circular and elliptic, and to emit energy when moving from one orbit to another of smaller size. These differences of opinion seem to us to indicate the gravity of the difficulties by which modern theories of the atom are surrounded. In the present state of our knowledge it is no doubt impossible to reconcile these theories with the postulates of the Theory of Atomic Form. The latter is based upon the conception of the reality of the existence of the atom, the variation of its form from atom to atom, throughout the Periodic Table, and in general the great stability of the individual atom itself," p. 5. What are Bohr, Lewis, and Langmuir in comparison with the eternal verities?

On p. 16 the author accepts the postulate that the isomer with the higher melting-point is the more stable. This is necessarily true, only in case there is but one form in the melt. On p. 33 the author discusses the relation of graphite to mellitic acid on the assumption that graphite can be oxidized to mellitic acid. This is very interesting, but can graphite be oxidized to mellitic acid?

Wilder D. Bancroft

Chemical Affinity. By L. J. Hudleston. 23 × 15 cm; pp. vi + 185. London: Longmans, Green and Co., 1928. Price: 7s. 6d. The latest addition to this excellent series of monographs deals with chemical affinity from a purely thermodynamic standpoint. The six chapters are entitled: Energy and its Transformations, Entropy, Free Energy, Solutions, The Nernst Heat Theorem and Third Law of Thermodynamics, Applications. The first and second chapters form a very condensed statement of the First and Second Laws of Thermodynamics, while the third and fourth chapters introduce the concept of activity and the methods and notation developed by G. N. Lewis. In the last chapter (27 pages) lies the main purpose of the book, which is the application of the previously derived theorems to the calculation of chemical equilibria, including examples which deal with the possibility of detecting experimentally new cases of equilibrium states. The author works through a score or so of problems which appear to be well chosen for the end in view. The basis of his calculations is the table (reproduced in an appendix) of free energy values computed by Lewis and Randall: "Thermodynamics and the Free Energy of Chemical Substances." The importance of the systemization of such data for predicting the direction and equilibrium conditions of chemical processes requires no advocacy, and the present work should serve as a useful commentary on the methods of utilizing free energy tables. Particularly helpful to the student are the clear recognition of the limitations of these methods in certain cases and the discussion in others of the effect of inaccuracies in the data employed. The reviewer has detected a few numerical and other errors in the text (for example on pages 33, 44, 64, 66, 79 and 112) and some readers might raise objections to certain ambiguous statements in the opening chapters. These are comparatively minor blemishes, however, and the book is one which can be recommended for use by researchers and senior students.

R. O. Griffith

CARBON DIOXIDE CLEAVAGE FROM ACETONE DICARBOXYLIC ACID*

BY EDWIN O. WIIG

Acetone dicarboxylic acid was first isolated by von Pechmann¹ in 1884. The acid is a white crystalline solid melting at 135°. It is very soluble in water and alcohol, less readily in ethyl acetate and still less in ether; insoluble in chloroform, benzene, and ligroin. On boiling acetone dicarboxylic acid with water, acids, or alkalies, it decomposes into acetone and carbon dioxide as represented by the equation:—



According to the literature the acid decomposes even at room temperature so that it is generally converted to the ethyl ester which is subsequently used in organic syntheses. However it was found that acetone dicarboxylic acid purified by crystallization from ethyl acetate and kept in a desiccator over phosphorus pentoxide for seven months (from March to October) showed no decomposition.

A study of the decomposition of acetone dicarboxylic acid in various solvents and with various catalysts was undertaken for the purpose of determining the mechanism of the reaction.

Experimental

Materials

The acetone dicarboxylic acid was prepared by several different methods but the method which gave the best yield is that described² in *Organic Syntheses*, Vol. V.

The acid thus obtained was recrystallized from ethyl acetate at least three times; it gave no test for sulfates, and melted sharply at 135°. The other substances used were all purified in accordance with standard methods.

Apparatus and Method of Procedure

The rate at which the acetone dicarboxylic acid decomposed was followed by measuring the volume of carbon dioxide evolved. The apparatus used was essentially of the type designed by Walton.³ The carbon dioxide evolved was conducted by capillary tubing to a calcium chloride tube which contained phosphorus pentoxide on glass wool to remove water or alcohol vapors and thence to a water-jacketed burette which was maintained at 25°. The gas was collected over paraffin oil rather than water since carbon dioxide

* Part of this paper was presented at the Seventh Midwest Regional Meeting at Chicago, May 27, 1927. This communication is an abstract of the thesis submitted to the Graduate School of the University of Wisconsin by Edwin O. Wiig in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work herein described was done under the direction of Professor J. H. Walton.

¹ von Pechmann: *Ber.*, 17, 2542 (1884).

² C. S. Marvel, Editor: "*Organic Syntheses*," 5, 5 (1925).

³ Walton: *Z. physik. Chem.*, 47, 185 (1904).

is appreciably soluble in water and only very slightly soluble in paraffin oil. As carbon dioxide is moderately soluble in the solvents used, they were saturated with dry carbon dioxide gas at the temperature of the experiment. To insure complete stirring of the reaction mixture shaking beads were used in all cases. In aqueous solutions short pieces of Bakelite rod were added, while in alcoholic solutions beads made of tin were employed since at 40° and 50° the alcohols attacked the Bakelite. Glass beads could not be used as it was observed that they catalyzed the reaction, due, no doubt, to the alkali which was dissolved from them.

Results

(a) *Completeness and Order of the Reaction.* Willstätter and Pfannenstiel¹ state that aniline decomposes acetone dicarboxylic acid catalytically and quantitatively into acetone and carbon dioxide. The procedure previously outlined was found to give 100% yield within the limits of experimental error. The yield of carbon dioxide when other catalysts were used or when the acid was decomposed in pure solvents, such as water and alcohols, was not found to be equal to the theoretical; this fact will be discussed later, however.

The order of the reaction for the decomposition of acetone dicarboxylic acid was found to be monomolecular in character. This was determined in two ways: (1) by the constancy of the velocity constants in any one experiment, and (2) by the constancy of the velocity constants with variation in the initial concentration of the acid. The velocity constants were calculated by substituting gas volumes for concentrations in the well-known formula for a unimolecular reaction.

(b) *The Effect of Acetone.* Since many reactions are auto-catalyzed, it was necessary to determine the effect of the decomposition products of acetone dicarboxylic acid on the rate of reaction. The sample of acetone dicarboxylic acid decomposed in all experiments weighed about 0.1450 g., which is equivalent to about 0.05 cc. of acetone. When twice this amount of acetone was added to the water in the reaction flask, the velocity constant ($K \times 10^4$) obtained was 182, while the average value for decomposition of the acid in water alone is $K \times 10^4 = 185$. Hence acetone has no appreciable effect on the velocity of the reaction.

(c) *The Effect of a Non-polar Lining.* Because of the possibility that alkali might be dissolved from the Pyrex flasks and catalyze the reaction, experiments were carried out in which the surface of the flasks was coated with paraffin. The Bakelite shaking rods, however, were not so treated. At the conclusion of the experiments the film of paraffin was found to be intact. That the character of the walls has practically no effect is shown by the following average velocity constants at 50°: $K \times 10^4 = 177$ for paraffin-coated walls and $K \times 10^4 = 185$ for glass walls.

(d) *Decomposition in Various Solvents.* The velocity of decomposition of acetone dicarboxylic acid in various solvents was measured in the hope of

¹ Willstätter and Pfannenstiel: Ann., 422, 1-15 (1920).

finding some relationship between the solvent and the reaction rate. The data obtained are given in Table I. The determinations were carried out principally at 40° and 50°, except in the case of aniline with which the reaction was so rapid that it could be followed only at 0°.

In order to compare the velocity of decomposition in mixed solvents with the results obtained by other investigators, five solutions containing various percentages of isopropyl alcohol and water were used as the reaction media. The results obtained are represented graphically by the curve in Fig. 1. It



FIG. 1
Reaction rate in isopropyl alcohol-water solutions at 40°C.

TABLE I
Reaction Rates in Various Solvents

Initial conc. of acetone dicarboxylic acid = 50 m. mol. per liter

| Solvent | K × 10 ⁴ | | | |
|----------------|---------------------|-----|-----|-----|
| | 0° | 40° | 50° | 60° |
| Methyl Alcohol | | 88 | | |
| Ethyl " | | 47 | 177 | |
| Propyl " | | 129 | 467 | |
| Isopropyl " | | 68 | 206 | |
| Butyl " | | 63 | 201 | |
| Isobutyl " | | 62 | 181 | |
| Isoamyl " | | 64 | 193 | |
| 85% Glycerine | | 70 | | |
| Water | | 57 | 185 | 548 |
| Aniline | 2420 | | | |

will be observed that small amounts of water catalyzed the decomposition of acetone dicarboxylic acid in alcohol, and conversely small quantities of alcohol accelerated the reaction in water. The reaction velocity reached a

maximum when the alcohol and water were present in approximately equimolecular ratio. In studying the decomposition of hydrogen peroxide in mixed alcoholic solvents, Bohnson¹ generally obtained a minimum in the reaction velocity instead of a maximum as in this work. There is apparently no relationship between the reaction rate and the known properties of solvents or mixed solvents. Bohnson came to the conclusion that the solvent exerts a specific effect, this effect being the resultant of a number of other effects, such as association of the solvent, viscosity, surface tension, dissociation of the catalyst and possible reaction between the solvent and the dissolved substance.

(e) *The Effect of Catalysts in Aqueous Solution.* Since aniline greatly increases the speed of decomposition of acetone dicarboxylic acid, a study of the effect of varying the concentration of the catalyst was made. Bredig,² in studying the decomposition of camphocarboxylic acid in organic solvents such as acetophenone, *o*-nitrotoluene, and *m*-xylene, found no relationship between the reaction rate and the dissociation constant of the nitrogen bases which he used as catalysts. On the other hand, Schierz³ found that tertiary nitrogen bases were active catalysts in the decomposition of formic acid in acetic anhydride solution and that the velocity of the reaction corresponded in a general way to the strength of the base. Primary and secondary bases, however, were not catalysts. These facts led to the reaction mechanism which he put forth to explain the decomposition of formic acid in acetic anhydride. With the hope that similar experiments would lead to a mechanism for the decomposition of acetone dicarboxylic acid, a study was made of the effect of various types of nitrogen bases on the reaction rate. The velocity constants obtained with aqueous solutions of aniline and of several other substances at various concentrations are represented graphically by the curves in Fig. 2. It will be observed that aniline is a much better catalyst than any of the others tried. There is no apparent relation between the strength of the base and its effect on the reaction rate. The velocity constants obtained with aniline, methyl aniline, and quinoline as catalysts at 50° at concentrations of 30 millimols per liter are respectively: 860, 300, 220; while their dissociation constants⁴ are respectively: 3.5×10^{-10} , 2.5×10^{-10} , 1.6×10^{-9} . Pyridine is about as efficient a catalyst as quinoline and has a dissociation constant of 2.3×10^{-9} .

(f) *The Effect of Catalysts in Alcohols.* The nitrogen base catalysts tried in aqueous solution indicated that there was no relationship between the strength of the base and the velocity of decomposition of acetone dicarboxylic acid. However, owing to limited solubility in water, few such bases were tried. The nitrogen bases are much more soluble in alcohols than in water, so that by studying their effect on the reaction rate in alcoholic solutions a

¹ Bohnson: *J. Phys. Chem.*, **24**, 677 (1920).

² Bredig: *Z. Elektrochemie*, **24**, 285 (1918).

³ Schierz: *J. Am. Chem. Soc.*, **45**, 455 (1923).

⁴ Scudder: "The Electrical Conductivity and Ionization Constants of Organic Compounds," (1914).

greater variety of these bases could be tried. Since the effect of aniline in aqueous solution had been studied, it was also of interest to study its effect in alcoholic solutions. Isopropyl alcohol was chosen as the solvent in most of the experiments with alcoholic solutions of catalysts, since a good supply of it was available and also because it can easily be obtained in an anhydrous condition.¹

The results obtained with aniline in isopropyl alcohol are represented graphically by curve A in Fig. 2. It will be observed that the curves for the velocity of decomposition of acetone dicarboxylic acid in alcohol and in water

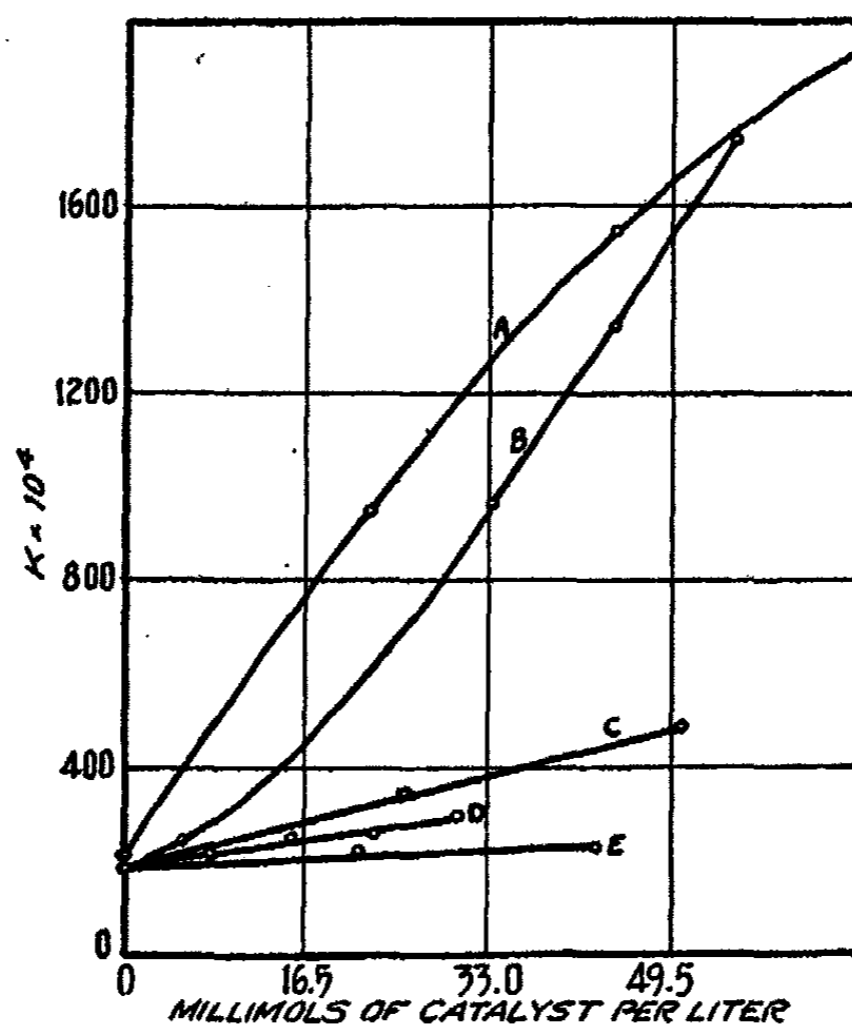


FIG. 2
Effect of catalysts on reaction rate at 50°C.

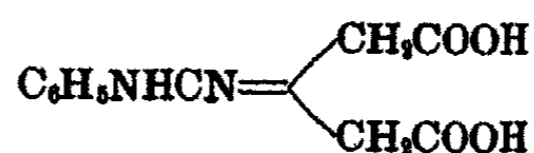
- A—Aniline in isopropyl alcohol
- B—Aniline in water
- C—Sulfanilic acid in water
- D—Methylaniline in water
- E—Quinoline in water

with aniline as a catalyst are of approximately the same magnitude, except that the former is concave downward and the latter concave upward. The curves cross each other at a concentration of aniline which is about equivalent to the concentration of the sample of acetone dicarboxylic acid decomposed.

Phenylhydrazine, in addition to being basic, also forms phenylhydrazones with ketones, etc. According to von Pechmann and Jenisch², phenylhydrazine and acetone dicarboxylic acid form a hydrazone of the formula:—

¹ Schuette and Smith: *Ind. Eng. Chem.*, 18, 1242 (1926).

² von Pechmann and Jenisch: *Ber.*, 24, 3253 (1891).



The velocity constants obtained with phenylhydrazine in isopropyl and isoamyl alcohols at several temperatures and concentrations are given in Table II.

TABLE II

Reaction Rate with Phenylhydrazine in Isoamyl and Isopropyl Alcohols
Initial conc. of acetone dicarboxylic acid = 50 m. mols per liter
Concentration of catalyst in millimols per liter of alcohol

| Temp. | Conc. of catalyst | $K \times 10^4$ | Temp. | Conc. of catalyst | $K \times 10^4$ |
|-------------------|-------------------|-----------------|-------------------|-------------------|-----------------|
| Isopropyl Alcohol | | | Isopropyl Alcohol | | |
| 10 | 40.6 | 663 | 40 | 50.8 | Too fast |
| 10 | 50.8 | 714 | Isoamyl Alcohol | | |
| 10 | 60.9 | 730 | 10 | 50.8 | 601 |
| 10 | 76.2 | 737 | 20 | 50.8 | 1750 |
| 20 | 50.8 | 2370 | 20 | 60.9 | 1750 |
| 30 | 50.8 | 6560 | 20 | 76.2 | 1750 |

Concentrations of catalyst below 50 millimols per liter (which correspond to a ratio of one mol of acid to one mol of catalyst) could not be used because the phenylhydrazine was used up by reacting with the acetone formed as a result of the decomposition of acetone dicarboxylic acid. With 10 millimols of catalyst to 50 millimols of acid about one-fifth of the acid decomposed rapidly and the remainder slowly. That the phenylhydrazine was used up by combination with acetone was also shown by using equimolecular quantities (50 millimols each per liter) of phenylhydrazine and acetone in isopropyl alcohol and then dropping into the solution the usual sample of acetone dicarboxylic acid. The speed of decomposition was too slow to measure at 10° whereas without the acetone the reaction proceeded rapidly. It will be observed that the velocity constant is almost constant for concentrations of phenylhydrazine in excess of 50 millimols. This would seem to indicate that the catalytic action is due to the formation of a phenylhydrazine intermediate compound and not to the formation of a salt by reaction between the carboxyl acid group and the phenylhydrazine acting as a base. If the catalyst forms intermediate compounds at the keto carbonyl group, then the catalytic activity should not be determined by the strength of the nitrogen base, but rather by the groups associated with the nitrogen atoms. That this is the case is shown clearly in Tables III and IV, which summarize the data obtained with various nitrogen compounds (and iodobenzene) as catalysts, both in aqueous and alcoholic solutions.

TABLE III
 Reaction Rate with Various Catalysts in Water
 Initial conc. of acetone dicarboxylic acid = 50 m. mols per liter
 Concentration of catalyst in millimols per liter of water
 Temperature = 50° $K \times 10^4$ for water at 50° = 185

| Catalyst | Conc. | $K \times 10^4$ | Dissociation ^a Constant of Base |
|-----------------|-------|-----------------|-----------------------------------------------|
| Aniline | 55 | 1734 | 3.5×10^{-10} |
| Aniline | 33 | 960 | 3.5×10^{-10} |
| Methylaniline | 30 | 295 | 2.5×10^{-10} |
| Quinoline | 42 | 230 | 1.6×10^{-10} |
| Pyridine | 62 | 200 | 2.3×10^{-9} |
| Sulfanilic Acid | 50 | 486 | 6.6×10^{-4} |
| Acetanilide | 50 | 203 | 4.4×10^{-14} |

^a From Seudder's "The Electrical Conductivity and Ionisation Constants of Organic Compounds," (1914).

^b Sulfanilic acid is an acid, not a base, hence this value is the acid dissociation constant.

TABLE IV
 Reaction Rate with Various Catalysts in Isopropyl Alcohol
 Initial conc. of acetone dicarboxylic acid = 50 m. mols per liter
 Concentration of catalyst in millimols per liter of alcohol
 $K \times 10^4$ for isopropyl alcohol at 50° = 206

| Catalyst | Conc. | Temp. | $K \times 10^4$ | Dissociation Constant of Base |
|------------------------|-------|-------|-----------------|----------------------------------|
| Phenylhydrazine | 50 | 30 | 6560 | 1.6×10^{-9} |
| p-Toluidine | 50 | 50 | 3750 | 1.6×10^{-9} |
| Aniline | 55 | 50 | 1740 | 3.5×10^{-10} |
| α Naphthylamine | 50 | 50 | 890 | 2.8×10^{-10} |
| Urea | 50 | 50 | 235 | 1.5×10^{-14} |
| Pyrrrol | 72 | 50 | 220 | — |
| Acetylphenylhydrazine | 50 | 50 | 216 | — |
| Diphenylamine | 50 | 50 | 219 | — |
| Quinoline | 42 | 50 | 645 | 1.6×10^{-9} |
| Dimethyl Aniline | 40 | 50 | 300 | 2.4×10^{-10} |
| Iodobenzene | 89.7 | 50 | 223 | — |

From an examination of the two preceding tables it will be observed that there is no relation between catalytic activity and the strength of the basic catalyst as measured by its dissociation constant. Furthermore, sulfanilic acid is a fair catalyst and yet functions as an acid in solution as evidenced by its acid dissociation constant. Of the reagents tried, all those which are efficient catalysts contain the amino group. Urea is not a catalyst, but in this compound the two amino groups are united with the negative carbonyl group. It seems then that the amino group is necessary for an efficient catalyst, but that the nature of the group combined with the amino radical also has considerable influence.

(g) *The Effect of Various Substances dissolved in Aniline.* Mention has already been made of the results obtained for the velocity of decomposition of acetone dicarboxylic acid in aniline as the solvent at 0° . In his study of the decomposition of malic acid in 100% sulfuric acid Whitford¹ found that the addition of various substances which formed molecular compounds with

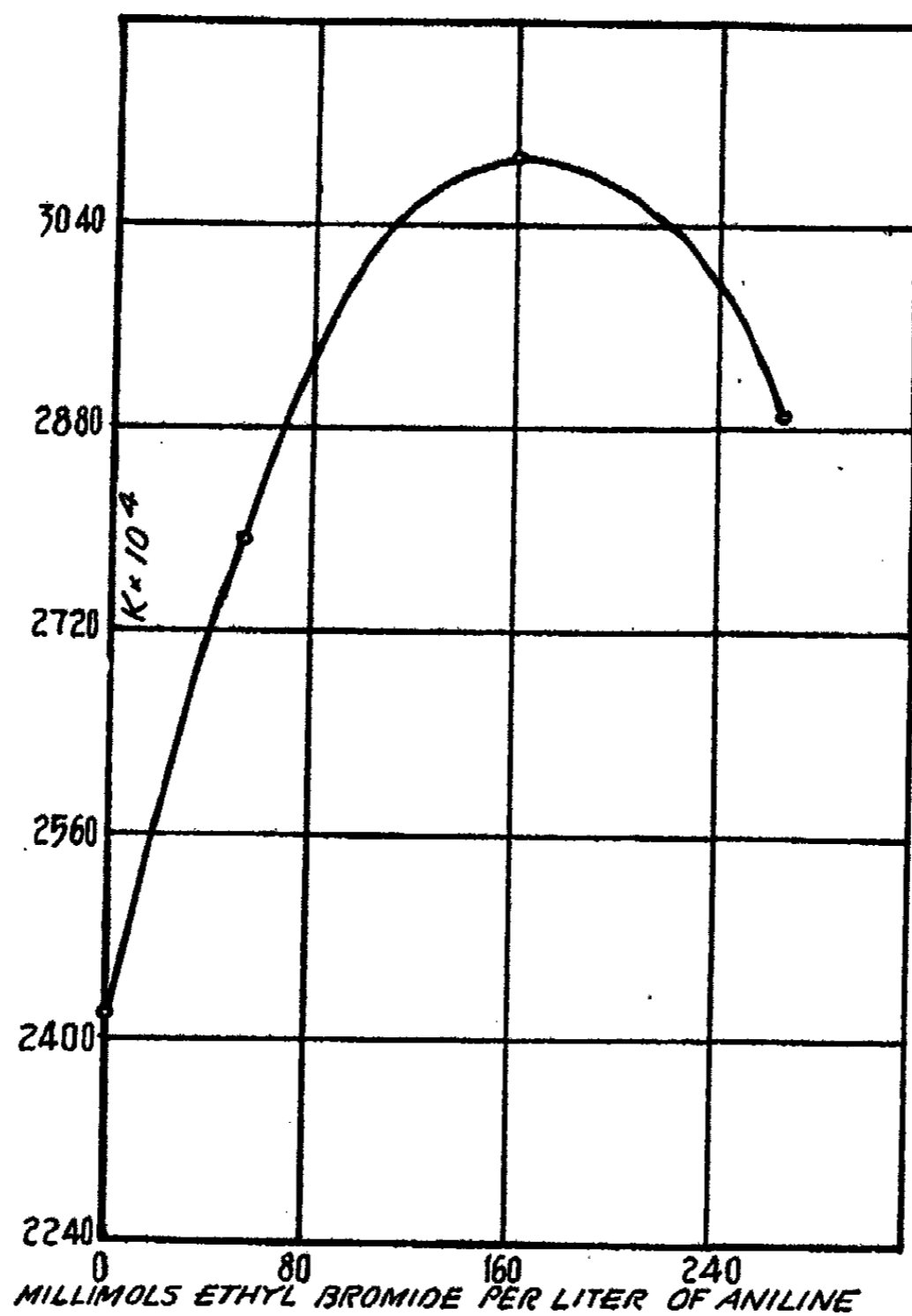


FIG. 3
Effect of ethyl bromide in aniline at 0°C .

sulfuric acid retarded the rate of decomposition. He postulated the formation of an unstable intermediate addition compound of sulfuric acid and malic acid and explained the behavior of the negative catalysts in accordance with Taylor's² theory of negative catalysis. According to this theory the inhibitor decreases the speed of a reaction by forming molecular compounds with the

¹ Whitford: *J. Am. Chem. Soc.*, 47, 953 (1925).

² Taylor: *J. Phys. Chem.*, 27, 322 (1923).

"active" molecules of either or both of the reactants. On this basis the addition of ethyl bromide to aniline should decrease the velocity of decomposition of acetone dicarboxylic acid in aniline, since ethyl bromide and aniline would form phenyl-ethyl-ammonium bromide. The opposite effect, however, was obtained, the velocity constant rising to a maximum and then falling off again as the concentration of ethyl bromide was increased. The data obtained are shown graphically in Fig. 3. The results obtained with the other substances tried in aniline solution are given in Table V. Since water dissolved in aniline was found to accelerate the decomposition of acetone dicarboxylic

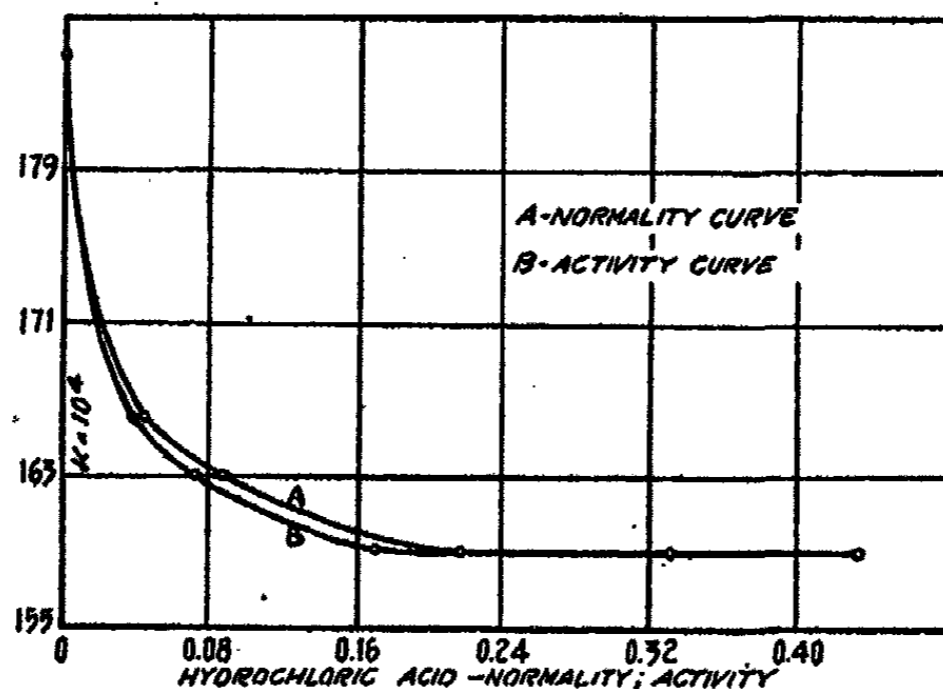


FIG. 4
Effect of hydrochloric acid on reaction rate at 50°C.

acid, the reaction media saturated with carbon dioxide at 0° were transferred to the shaking flasks without exposure to the moist air of the laboratory.

TABLE V
Reaction Rate with Various Substances Dissolved in Aniline at 0°
Initial conc. of acetone dicarboxylic acid = 50 m. mols per liter
Concentration of catalyst in millimols per liter of aniline

| Catalyst | Concentration $K \times 10^4$ | Catalyst | Concentration $K \times 10^4$ |
|-----------------|-------------------------------|-----------------------------------|-------------------------------|
| Water | 278 | Acetic Anhydride (Acetanilide) | 106 |
| | 2830 | | 2830 |
| Mercuric Iodide | 75 | None | — |
| Dextrose | 25 | | 2420 |
| | 3240 | | |

(h) *The Effect of Hydrochloric Acid.* The rate of decomposition of acetone dicarboxylic acid with various concentrations of hydrochloric acid in water was measured to determine the effect of hydrogen ion concentration on the reaction rate. It was found that the velocity constant at first decreased and then remained constant with increasing concentration of hydrochloric acid. The results obtained in these experiments at 50° are represented graphi-

cally by the curves in Fig. 4. A study of the data reveals the fact that concentrations of hydrochloric acid greater than 0.05 Normal (the molecular equivalent of the acetone dicarboxylic acid present) have very little added effect in retarding the reaction. This may indicate the formation of an intermediate molecular compound of hydrochloric acid and acetone dicarboxylic acid which is somewhat more stable than the acetone dicarboxylic acid in water. It will be observed that the curve for velocity constant plotted against normality of hydrochloric acid is identical with the one obtained if normality is replaced by activity.¹ It must be remembered that the velocity constant at zero normality hydrochloric acid is the velocity constant for water saturated with carbon dioxide at 50° and that the latter solution consequently contains a small but definite hydrogen ion concentration. Since the curve shows that the velocity constant increases with decreasing hydrogen ion concentration, it is probable that $K \times 10^4$ in pure water would be higher than 185, the value found for water saturated with carbon dioxide at 50°.

(i) *The Effect of Various Salts.* The effect of salts on the decomposition of acetone dicarboxylic acid in water is interesting. Ordinary neutral salts, such as potassium bromide, sodium nitrate, and sodium chloride, have practically no effect on the velocity of decomposition, whereas sodium sulfate, which is generally considered neutral, accelerates the reaction slightly. Similarly, salts which on hydrolysis give an alkaline reaction also increase the reaction rate. If to a solution of sodium bicarbonate at 50° acetone dicarboxylic acid is added in equimolecular ratio, about 65% of the acid decomposes immediately while the remainder decomposes slowly, as it would in water alone. In like manner tri-sodium and di-sodium phosphate solutions decompose respectively about 75% and 45% of the acid immediately while the rest of the acid decomposes slowly. The velocity constants obtained with various salts are given in Table VI. The velocity constant increases as the strength of the acid from which the salt is derived decreases. This also determines the degree of hydrolysis of the salt, hence it may be said that the greater the alkalinity at a given concentration of salt, the greater the accelerating effect on the velocity of decomposition of acetone dicarboxylic acid. Salts showing an acid reaction on hydrolysis would undoubtedly decrease the reaction rate since that is the effect produced by hydrochloric acid.

The above salt solutions, however, are acid rather than alkaline in reaction because of the carbon dioxide present. The hydrogen ion concentration of four of them was determined by a hydrogen electrode with the following results:—sodium acetate solution, pH = 6.3; sodium oxalate solution, pH = 6.3; sodium sulfate solution, pH = 4.8; sodium diacid phosphate solution, pH = 3.1. While these values are somewhat in error because of the difficulty in making accurate hydrogen ion concentration measurements at such low (0.05 molar) salt concentrations, the results show, nevertheless, that the so-

¹ The activity coefficients of hydrochloric acid were obtained by interpolation from the values given on page 336 of "Thermodynamics and The Free Energy of Chemical Substances" by Lewis and Randall, (1923). While these values are for 25° and would be somewhat different at 50°, the relative order of the activity coefficients would be the same.

lutions are acidic in reaction and that the lower the acidity the greater the velocity constant. If the curve for the change of the velocity constant with change in concentration of hydrochloric acid could be continued to the hydrogen ion concentration of pure water ($\text{pH} = 7.0$), the values given by the salt solutions would probably fall on the curve (Fig. 4).

TABLE VI
Reaction Rate with Salts in Water
Initial conc. of acetone dicarboxylic acid = 50 m. mols per liter
Concentration of salt in millimols per liter of water

| Salt | Conc. | Temp. | $K \times 10^4$ | Salt | Conc. | Temp. | $K \times 10^4$ |
|--------------------------|-------|-------|-----------------|------------------------------------|-------|-------|-----------------|
| None | 0 | 40 | 57 | KBr | 50 | 50 | 184 |
| Na_2SO_4 | 50 | 40 | 63 | Na_2SO_4 | 50 | 50 | 200 |
| K_2SO_4 | 50 | 40 | 65 | NaH_2PO_4 | 50 | 50 | 205 |
| None | 0 | 50 | 185 | $\text{Na}_2\text{C}_2\text{O}_4$ | 50 | 50 | 242 |
| NaCl | 50 | 50 | 180 | $\text{NaC}_2\text{H}_3\text{O}_2$ | 50 | 50 | 275 |
| NaNO_3 | 50 | 50 | 184 | $\text{NaC}_2\text{H}_3\text{O}_2$ | 33.7 | 50 | 249 |

(j) *The Effect of Colloids.* According to Findlay and Thomas¹ the presence of colloids in a solution decreases the rate at which gases are evolved, so that if the velocity of a chemical reaction is followed in this way the measurements are in error. In this laboratory, Pray,² in studying the decomposition of diazobenzene chloride, found that collodion had no effect on the reaction rate. It was of interest, therefore, to determine the effect of colloids on the rate of decomposition of acetone dicarboxylic acid. Solutions of virtually the same colloids and the same concentrations as Findlay and Thomas had used were also employed in these experiments. The data obtained for the velocity constants are tabulated in Table VII.

TABLE VII
Reaction Rate in Aqueous Colloidal Solutions at 40°
Initial conc. of acetone dicarboxylic acid = 50 M. mols per liter

| Colloid | Conc. Percent | Age of Solution | $K \times 10^4$ | Colloid | Conc. Percent | Age of Solution | $K \times 10^4$ |
|---------|---------------|-----------------|-----------------|-------------|---------------|-----------------|-----------------|
| None | — | — | 57 | Gelatin | 2 | 3 days | 80 |
| Starch | 1 | 1 day | 58 | " | 3 | 3 " | 106 |
| " | 2 | 1 " | 57 | " | 3 | fresh | 92 |
| " | 3 | 1 " | 59 | Egg Albumin | 1 | 2 days | 87 |
| " | 3 | fresh | 58 | Agar | 2 | fresh | 64 |

(almost a gel)

It will be observed that starch has no effect on the velocity of the reaction, which agrees with the work of Pray, while the other colloids employed speed up the reaction. The 2% agar solution was practically set to a gel and yet it

¹ Findlay and Thomas: *J. Chem. Soc.*, 119, 170 (1921); 125, 1244 (1924).

² Pray: *J. Phys. Chem.*, 30, 1482 (1926).

did not decrease the velocity of the reaction. With the exception of starch, the colloids used are protein compounds and probably contain the amino group. This probably accounts for their catalytic action and also for the in-

TABLE VIII

Effect of Temperature on the Reaction Rate in Water
Initial conc. of acetone dicarboxylic acid = 50 m. mols per liter
Concentration of catalyst in millimols per liter of water

| Temp. | Catalyst | Conc. | $K \times 10^4$ | Temp. Coefficient | Critical Increment (E) |
|-------|----------|-------|-----------------|-------------------|------------------------|
| 40 | — | — | 57 | | |
| 50 | — | — | 185 | 3.25 | 23,600 |
| 60 | — | — | 548 | 2.96 | 23,100 |
| 40 | Aniline | 44 | 502 | | |
| 50 | " | 44 | 1350 | 2.68 | 19,700 |
| 50 | " | 16.5 | 463 | | |
| 60 | " | 16.5 | 1190 | 2.57 | 19,200 |

TABLE IX

Effect of Temperature on the Reaction Rate in Alcohols
Initial conc. of acetone dicarboxylic acid = 50 m. mols per liter
Concentration of catalyst in millimols per liter of solvent

| Temp. | Alcohol | Catalyst | Conc. | $K \times 10^4$ | Temp. Coefficient | Critical Increment (E) |
|-------|-----------|-----------------|-------|-----------------|-------------------|------------------------|
| 40 | Ethyl | — | — | 47 | | |
| 50 | " | — | — | 177 | 3.77 | 26,600 |
| 40 | Propyl | — | — | 129 | | |
| 50 | " | — | — | 467 | 3.62 | 25,800 |
| 40 | Isopropyl | — | — | 68 | | |
| 50 | " | — | — | 206 | 3.03 | 22,200 |
| 40 | Butyl | — | — | 63 | | |
| 50 | " | — | — | 201 | 3.19 | 23,200 |
| 40 | Isopropyl | — | — | 62 | | |
| 50 | " | — | — | 181 | 2.92 | 21,500 |
| 40 | Isoamyl | — | — | 64 | | |
| 50 | " | — | — | 193 | 3.02 | 22,100 |
| 30 | Isopropyl | Aniline | 66 | 688 | | |
| 40 | " | " | 66 | 1170 | 1.70 | 9,970 |
| 50 | " | " | 66 | 1930 | 1.65 | 10,000 |
| 10 | Isoamyl | Phenylhydrazine | 50.8 | 601 | | |
| 20 | " | " | 50.8 | 1750 | 2.91 | 17,500 |
| 10 | Isopropyl | " | 50.8 | 714 | | |
| 20 | " | " | 50.8 | 2370 | 3.32 | 19,700 |
| 30 | " | " | 50.8 | 6560 | 2.77 | 17,900 |

creased catalytic activity of a three days old solution over a fresh solution since hydrolysis and decomposition would take place on standing.

(k) *The Effect of Temperature on the Reaction Rate.* The data for the effect of temperature on the velocity of decomposition of acetone dicarboxylic acid are assembled in Tables VIII and IX. From an examination of the tables it will be seen that the temperature coefficient always decreases with increase in temperature and that the temperature coefficient for the reaction in a pure solvent is always higher than the value obtained when a catalyst is added.

The effect of temperature (T) on the velocity constant (k) has been expressed by Arrhenius in the equation $\frac{d \ln k}{d T} = \frac{E}{RT^2}$. The integrated form of this equation, $E = \frac{1.98 T_2 T_1 \times 2.303 \log k_2/k_1}{T_2 - T_1}$, where E is expressed in

calories, was used to calculate the values for E, the "critical increment". The latter is defined by Tolman¹ as the difference between the average energy of the molecules and modes of electromagnetic vibration which actually take part in the reaction, and the average energy of those same elements whether or not they are in a reactive state. The critical increment should vary but slightly with temperature. An examination of the preceding tables will show this to be true for any single solvent, such as water, or for any one catalyst in a given solvent, as aniline in water or phenylhydrazine in alcohol. However, the values obtained for the critical increment vary greatly with the solvent and also with the catalyst.

TABLE X
Percentage Yield of Carbon Dioxide from Kinetic Measurements

| Temp. | Reaction Medium | Percent Yield |
|-------|-----------------------------|---------------|
| 60 | Water | 100 |
| 60 | Water and Aniline | 100 |
| 50 | Water | 97 |
| 50 | Water and Aniline | 100 |
| 50 | Alcohols | 97 |
| 50 | Alcohols and Water | 98 |
| 40 | Water | 92 |
| 40 | Alcohols | 95 |
| 40 | Alcohol and Aniline | 98 |
| 40 | Alcohol and Phenylhydrazine | 99 |
| 30 | Alcohol and Aniline | 96 |
| 30 | Alcohol and Phenylhydrazine | 92 |
| 20 | Alcohol and Phenylhydrazine | 89 |
| 10 | Alcohol and Phenylhydrazine | 89 |
| 0 | Aniline | 89 |

¹ Tolman: J. Am. Chem. Soc., 42, 2506 (1920).

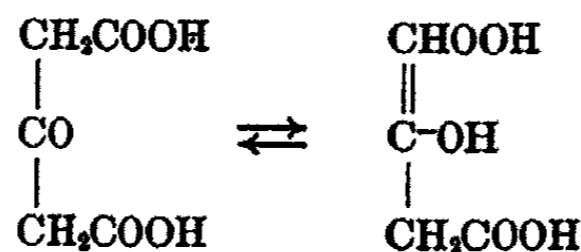
(1) *Measurements of Percentage Yield.* While studying the kinetics of the decomposition of acetone dicarboxylic acid, it was observed that the yield of carbon dioxide obtained was not always even approximately equal to the theoretical. At temperatures of 50° and 60° the amount of carbon dioxide evolved is about equal, within the limits of experimental error, to that calculated from the sample of acid decomposed. The yield when the acetone dicarboxylic acid is decomposed in pure solvents, dropped to about 92-95% at 40°, but the yield with catalysts was still approximately 100%. The reaction could not be followed by the gasometric method in water or alcohols at 30° or below because the reaction proceeded too slowly, but with catalysts at these lower temperatures measurements could easily be made. The yield of carbon dioxide at 30° and below, in the presence of catalysts, fell off considerably as will be observed by an examination of Table X, which gives the average yields of several experiments.

To check the above results a series of experiments was carried out using the following procedure in which the carbon dioxide was determined by an entirely different method. A half gram sample of acetone dicarboxylic acid in a hard glass capsule was dropped into 10 cc. of an isoamyl alcohol solution of the catalyst in a 6" × 1½" Pyrex test tube. The latter was supported in a thermostat at the desired temperature and nitrogen was passed through it to sweep out the carbon dioxide. The gases were then passed through a tube of calcium chloride (through which carbon dioxide had previously been passed to react with any lime or basic chloride present) to remove any alcohol vapors which would otherwise have been absorbed by the potash solution which followed. Isoamyl alcohol was used because of its low vapor pressure (9.7 mm. of mercury at 40°) since with ethyl alcohol as the solvent an appreciable error was introduced by the absorption of the alcohol vapors by the potash solution. Tin shaking beads were used to prevent supersaturation and the tube was shaken vigorously before the nitrogen was swept through it.

Due to the slight solubility of carbon dioxide some of the gas was retained by the alcoholic solution. This was corrected for by titrating the carbon dioxide in a similar solution saturated with the gas at the temperature of the experiment. Titrations were made by adding excess standard barium hydroxide solution and back titrating with oxalic acid solution.

The procedure was tested by determining the yield of carbon dioxide from the decomposition of acetone dicarboxylic acid in isoamyl alcohol with aniline as the catalyst at 40°. Two experiments gave an average of 99.4%, indicating that the method was sufficiently reliable.

The low yields of carbon dioxide previously mentioned might be due to the presence in solution of two forms of acetone dicarboxylic acid as illustrated by the following formulas:



The keto form of the acid would be expected to react with phenylhydrazine to form a hydrazone which would not occur with the enol form. If the enol form changes only very slowly to the keto form, then the preceding statement would suggest a method of determining the concentration of the two forms present. In the kinetic studies made at 10° when the ratio of phenylhydrazine to acetone dicarboxylic acid was 1 mol to 1 mol, the yield of carbon dioxide was 89% of the theoretical, while when the ratio was made 1.5 mols of catalyst to 1 mol of acid, the yield was 95%. Hence in the following experiments the ratio of phenylhydrazine to acetone dicarboxylic acid was equimolecular so that the excess of catalyst over the amount necessary to react with the keto form would be small. A large excess of catalyst might cause an acceleration in the rate at which the enol form is changed to the keto form, or perhaps cause the decomposition of the enol form. The data obtained in these experiments are tabulated in Table XI where the percentages given are the averages of two experiments.

TABLE XI
Percentage Yield of Carbon Dioxide
Concentration of Catalyst = 1 Mol
Concentration of Acid = 1 Mol

| Temp. | Time in Hours | Percent Yield | Time in Hours | Percent Yield |
|-------|---------------|---------------|---------------|---------------|
| 0 | 9 | 92.3 | 24 | 97.0 |
| 10 | 5 | 88.0 | 18 | 97.3 |
| 20 | 4 | 89.0 | — | — |
| 30 | 3 | 92.3 | — | — |
| 40 | 1 | 85.0 | 3 | 98.0 |

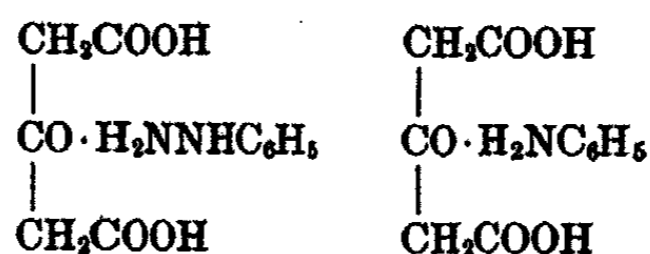
It will be observed in the above table that the decomposition is practically complete if the reaction is allowed to proceed long enough. The first column of percentage yields given in the table was determined after a time interval which was two to three times as long as the time necessary for 255/256 of the acid to have decomposed. This latter time was calculated from the kinetic measurements previously made in which the time for 50% decomposition was observed experimentally. The time for 75% decomposition as calculated from the time for 50% decomposition always checked with the experimentally determined time for 75% decomposition, which would seem to indicate that the calculation of the time for 255/256 decomposition is valid. Moreover, as has already been mentioned, at least twice as much time as this was allowed to elapse before the yield of carbon dioxide was determined, so that the reaction should certainly have been practically complete. From the results obtained it would seem that about 89% of the acid, when in solution at temperatures ranging from 0° to 40°, is in one form, probably the keto form, and the remaining 11% in the other form. It is most likely the keto form which is present to the extent of 89% since it seems more probable that the phenylhydrazine would react with it rather than with the enol form. There is, of

course, the possibility that some side reaction takes place in addition to the main reaction and that the product formed subsequently decomposes. This hypothesis seems improbable since aniline, which caused about 100% decomposition at 40° and higher temperatures, gave only a 96% yield at 30°. Aniline was not used in these experiments because, unlike phenylhydrazine, it is not used up during the reaction, so that after all the keto form had been decomposed there would be present a large excess of aniline which might catalyze the transformation of the enol to the keto form (or its decomposition). The mean value of 89% obtained in these experiments agrees well with the values obtained from kinetic measurements. The experimental error is large so that this value is only approximate. The possible explanations for the decrease in the yield of carbon dioxide will be discussed in another part of this paper.

Discussion

Mechanism of the Reaction

The catalytic decomposition of acetone dicarboxylic acid may be explained by the assumption that an unstable intermediate compound is formed by the addition of the catalyst to the keto carbonyl group of the acid. When phenylhydrazine and aniline are used as catalysts, the intermediate compounds would be

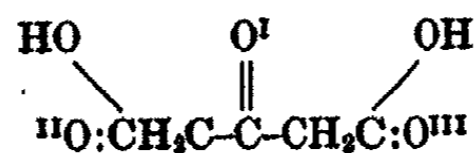


There are several reasons for believing such an assumption to be valid.

First, the intermediate compound is probably formed by the union of one molecule each of catalyst and acetone dicarboxylic acid, rather than two molecules of one to one molecule of the other. This is what would be expected on a basis of probability, since bimolecular collisions would occur much more frequently than termolecular collisions. Furthermore, when phenylhydrazine is used as a catalyst, if the ratio of catalyst to acetone dicarboxylic acid is less than one mol to one mol, only part of the acid is catalytically decomposed since the phenylhydrazine is used up by a secondary reaction with the acetone. If to 50 millimols of acetone dicarboxylic acid per liter of isopropyl alcohol at 10° concentrations of 50.8, 60.9, and 76.2 millimols of phenylhydrazine are added, the velocity constants ($K \times 10^4$) obtained are 714, 730, and 737, respectively. This indicates that, in the case of phenylhydrazine, the ratio of 1 mol of catalyst to 1 mol of acid is required, since greater concentrations of catalyst have very little added effect and smaller concentrations do not give complete decomposition. Finally, according to von Pechmann and Jenisch,¹ acetone dicarboxylic acid and phenylhydrazine react to form a hydrazone of the formula $\text{C}_6\text{H}_5\text{NHN}:\text{C}(\text{CH}_2\text{COOH})_2$. The two molecules undoubtedly first form a complex which then loses a molecule of water.

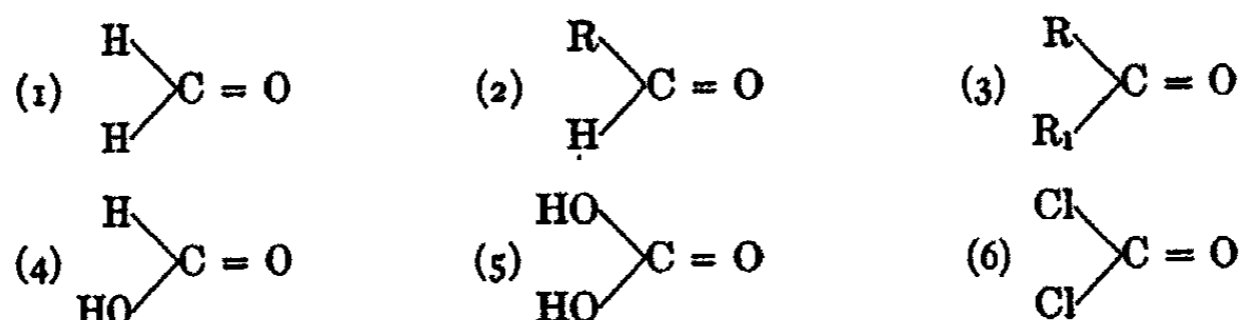
¹ von Pechmann and Jenisch: Ber., 24, 3253 (1891).

On examining the formula for acetone dicarboxylic acid, it will be observed that there are three carbonyl oxygen atoms present, numbered I, II, and III in the following formula:



Those numbered II and III are alike in that they are associated with an acid carboxyl group. Since most of the catalysts used are nitrogen bases, it might be supposed that the intermediate compound formed is a salt, due to reaction of the base with acid carboxyl group. However, a study of Tables III and IV will show this hypothesis to be untenable since bases of the same strength show far different catalytic activity and conversely, substances which are active catalysts vary in basic strength. Moreover, sulfanilic acid is a fair catalyst and yet it is acidic in reaction.

There is one more reason for believing that the intermediate compound formation takes place at carbonyl oxygen I, rather than II or III. Tschelinzeff,¹ from a study of heats of formation, has shown that the secondary valences of carbonyl oxygen decrease in strength in the order given in the following compounds of various structures:



The ketone group in acetone dicarboxylic acid would correspond to type (3) and the acid carboxyl groups to type (4), hence the secondary valences of the former are stronger. Of all the catalysts tried only those are active which contain the NH_2 group. Those catalysts which contain the secondary NH group or the N group are weak catalysts. Tschelinzeff² has also shown that the secondary valences of nitrogen are strongest in primary amines, weaker in secondary amines, and weakest in the tertiary amines. It would seem then that the intermediate compound formation is due to the attraction of the secondary valences of the nitrogen of the catalyst for the secondary valences of the carbonyl oxygen of the acid. Since the secondary valences of the keto carbonyl oxygen are stronger than those of the acid carboxyl group oxygen, the intermediate compound must be formed at the former. Furthermore, in the case of catalysts which contain the secondary or tertiary amino grouping, the secondary valences are weaker than in the primary amines; hence the former are weak catalysts. It will be remembered, however, that urea (NH_2CONH_2) was a weak catalyst and yet it contains two amino groups. The

¹ Tschelinzeff: Bull., 37, 181 (1925).

² Tschelinzeff: Bull., 37, 176 (1925).

probable reason for this is that the amino groups are already united with a carbonyl group and the secondary valences of the two nitrogen atoms and the oxygen atom have formed a stable configuration.

The formation of an unstable intermediate compound would also be predicted on the basis of the theory of molecular combinations proposed by Martinet and Bornand.¹ They divide organic compounds into "acidoids" and "basoids," the former being chromophores or substances constitutionally unsaturated and containing such groups as CO, CN, NO₂, etc., which are characterized by the presence of multiple valence bonds, while the latter are auxochromes or substances atomically unsaturated and contain such groups as OH, SH, NH₂, etc. The molecules are assumed to be polar and the fields of electric force, which are centered in the characteristic groups, are responsible for the electrical attraction which brings the acidoid and basoid into a complex. Acetone dicarboxylic acid would be classed as an acidoid and the catalysts and alcohols used would fall in the group of basoids. This theory, however, does not indicate the relative strengths of the various catalysts as well as the theory of Tschelinzeff.

The instability of the intermediate compound is best explained by recourse to the electronic conception of matter. As has already been indicated, the formation of the intermediate is due to the attraction between the partial valences of the nitrogen of the catalyst and the keto oxygen of the acid. In terms of electrons this would mean that the nitrogen and oxygen atoms tend to share electrons. This sharing of the electrons would probably cause a shifting of the electrons throughout the entire chain of carbon atoms in the acid and result in a strained condition of the molecule which subsequently causes its decomposition.

The mechanism of the decomposition of acetone dicarboxylic acid already outlined may be extended to its decomposition in pure solvents. In pure aniline at 0° the acid decomposes in a few minutes. The decomposition in water and alcohols at 40 and 50° is very much slower than in aniline at 0°. Likewise, according to Tschelinzeff, the partial valence of nitrogen in the amines is much stronger than that of the oxygen in the alcohols, which is in accord with the observed variations in the velocity of decomposition. Again the intermediate compound would be expected to be formed at the keto oxygen since its secondary valences are stronger than those of the carbonyl oxygen in the carboxyl acid groups.

All the alcohols might be expected to give approximately the same velocity constant, but this is not the case, as is shown by a glance at Table I. Further study reveals the fact that the velocity constant is higher for the normal alcohols containing an odd number of carbon atoms than for those with an even number of carbon atoms. Also the velocity constant increases in going from an alcohol of lower odd or even numbered carbon atoms to the next higher alcohol of odd or even numbered carbon atoms, respectively. This is in accord with the hypothesis of Cuy² who assumes that the carbon atoms in a chain

¹ Martinet and Bornand: *Rev. gen. sci.*, 36, 659 (1925).

² Cuy: *J. Am. Chem. Soc.*, 42, 503 (1920).

have a natural tendency to appear alternately positively and negatively charged. As a result, carbon compounds containing an odd number of carbon atoms would be expected to form one homologous series and those with an even number of carbon atoms a second homologous series. This may explain the variations in the physical properties of such homologous series and also the variation in the rates of reaction obtained in this work.

There may be some objection to the hypothesis that the alcohol forms an addition product at the keto group, since an alcohol and an acid would ordinarily be expected to form an ester. This objection may be met in two ways. In the first place the di-ethyl ester of acetone dicarboxylic acid is very much more stable than the acid itself. Secondly, to make this ester the mere bringing together of the alcohol and the acid is not sufficient; the anhydrous alcohol must be saturated with dry hydrogen chloride. According to Tschelinzeff, strong mineral acids, such as hydrogen chloride, would be expected to add to carbonyl oxygen. In the preparation of the ester then, the hydrogen chloride may first add at the keto group of the acid which would leave the weaker carboxyl group for the alcohol. On the addition of water to the reaction mixture the hydrogen chloride would be set free again. Such an explanation as the above would hold only if it is assumed that the hydrogen chloride addition compound is stable. That this assumption is valid is shown by the experimentally observed fact that hydrogen chloride decreases the velocity of decomposition of acetone dicarboxylic acid in water. From the standpoint of the sharing of electrons, the formation of the hydrogen chloride-acetone dicarboxylic acid complex would cause a shift in the electrons so that the strain which is normally present in the molecule would be relieved.

The hypothesis may be extended to explain the effect of salts on the rate of decomposition in aqueous solution. It will be remembered that the rate of reaction was determined, not in pure water, but in water saturated with carbon dioxide. The carbonic acid present would be expected to cause the reaction to proceed slower than in pure water, just as hydrogen chloride does, but to a smaller extent. The addition of slightly basic salts decreases the hydrogen ion concentration, hence decreases the retarding effect of the acid. Qualitative experiments indicated that the hydroxyl ion would have been found to be a positive catalyst if the experiments could have been conducted in alkaline solutions.

The intermediate compound theory proposed may be extended to the catalysts used in aniline solutions and also to explain the effect of colloids on the reaction rate. Starch, it will be recalled, had no effect on the reaction rate, which agrees with the work of Pray¹ but is contrary to the observations of Findlay and Thomas.² However, the other colloids used were protein products; hence they would be expected to catalyze the reaction because of the presence of the amino groups in their molecules.

¹ Pray: *J. Phys. Chem.*, **30**, 1482 (1926).

² Findlay and Thomas: *J. Chem. Soc.*, **125**, 1244 (1924).

According to Matière and Lumière,¹ chemical catalysts, that is, those which form intermediate compounds, decrease the sensitiveness of the reaction to temperature. This is in agreement with the results obtained with aniline and phenylhydrazine, both strong catalysts. These compounds gave lower temperature coefficients than were obtained with pure solvents.

Percentage Yield of Carbon Dioxide

In commenting on the percentage yields of carbon dioxide obtained from the decomposition of acetone dicarboxylic acid at temperatures below 40°, it was pointed out that a possible explanation for these low yields (about 89%) is that the acid is present in solution in two tautomeric forms—the enol and the keto forms. The keto form would be expected to react with a catalyst, like phenylhydrazine, while the enol form would not, and if the rate of change of the enol to the keto were small, the percent of the two tautomeric forms could be calculated. The structure of acetone dicarboxylic acid is analogous to that of aceto-acetic acid, so that the assumption of an enol and keto form is a possibility. Furthermore, ferric chloride gives an intense violet coloration to an aqueous solution of acetone dicarboxylic acid which is supposed to be a test for an hydroxy compound. This last observation, however, is not a sure indication of the presence of the enol form in solution, since the coloration might be brought about in some other way.

Professor Homer Adkins of this laboratory has pointed out that there are at least three other possible explanations for the decrease in percentage yield to 89% or for the slow decomposition of the last 11% of acetone dicarboxylic acid. From the available data it is impossible to say which of the four possible explanations is correct, although two of them seem highly improbable.

The slow decomposition of the last 11% of acetone dicarboxylic acid may be due to a poisoning of the catalyst at the lower temperatures. This poisoning of the catalyst becomes negligible at higher temperatures, so that approximately the theoretical yield is obtained. This explanation seems untenable, however, when it is observed that there is such a sharp break in the reaction, approximately 89% of the acetone dicarboxylic acid decomposing rapidly and the remainder very slowly. If the catalyst were being poisoned, a gradual falling off in the reaction rate would be expected.

The results obtained might also be accounted for by the assumption that the active mass of the acetone dicarboxylic acid may not have been what it appeared to be. The velocity constants were calculated by assuming "a" in the formula for a monomolecular reaction to be equal to the number of cc. of gas evolved when the reaction appeared to be complete. Any error in "a", would cause an error in the calculation of the time necessary for 100% decomposition, and the calculation of the percents of the tautomeric forms is based on the assumption that the reaction has had time enough to go to completion. This error would seem to be small, however, as it makes a difference of only two minutes in the time of half life at 10°. Five hours were allowed to elapse before the percentage yield of carbon dioxide was determined at 10°.

¹ Matière and Lumière: *Ann. Phys.*, 11, 53 (1919).

which was almost four times that required by calculations, so that any error in the assumption of the active mass of acetone dicarboxylic acid should have been more than compensated by the large excess of time allowed.

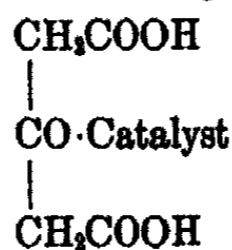
The fourth possible explanation for the extremely slow decomposition of the last 11% of the acetone dicarboxylic acid is more probable. Lower temperatures may favor the formation of salts rather than the ketone addition compounds formed at higher temperatures. The assumption that these salts are formed to the extent of about 11% and that they decompose very slowly would account for the results obtained.

Thus, while the percentage yields may be interpreted by assuming the presence of the tautomeric enol and keto forms, another explanation is possible.

The writer wishes to express his appreciation of the kindly interest and helpful guidance of Professor J. H. Walton, under whose direction this work was performed.

Summary

1. The decomposition of acetone dicarboxylic acid is a reaction of the first order.
2. The reaction rate is practically independent of the nature of the walls of the reaction flask.
3. Acetone, a product of the decomposition, has practically no effect on the velocity.
4. The velocity of decomposition has been measured in water, aniline, and various alcohols.
5. The effect of catalysts dissolved in water, aniline, and alcohols on the reaction rate has been determined.
6. Observations have been made of the effect of hydrochloric acid and various salts on the rate of decomposition in aqueous solution.
7. The effect of colloids on the velocity of decomposition in water has been studied.
8. Temperature coefficients for the various alcohols, for water, and for catalysts in alcohols and water have been calculated.
9. Measurements of the completeness of the decomposition in various solvents, with and without catalysts, have been made at temperatures ranging from 0° to 60°.
10. A mechanism for the reaction has been proposed, postulating the formation of an unstable intermediate compound of the formula



11. The possible explanations for the decrease in the percentage decomposition of the acid with decrease in temperature are discussed.

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THE SECOND LAW OF THERMODYNAMICS IN CHEMISTRY

BY R. C. CANTELO

The Second Law of Thermodynamics is one of the most precious of the laws of chemistry as well as of the other sciences. Its statement, however, is usually such that its fundamental nature in chemistry is concealed. Such expressions as: Heat of itself cannot flow from a lower to a higher temperature; the entropy of an isolated system tends always to increase; the mathematical expression derived from Carnot's cycle; and even the more readily grasped idea that in equilibrium, the free energy is a minimum at constant temperature and pressure; do not reveal themselves as of importance to chemical science.

The fundamental idea of the Second Law is given by the statement: Heat cannot be converted into work *without compensation*; and from this expression of the Law, follow all the ideas as expressed above.

There are two possible cases:

1. Heat is converted into work at constant temperature, i.e., an isothermal process by which heat is converted into work. What is the compensation? This can best be made clear by examples.

(a) A compressed perfect gas expands isothermally and does work. The initial state of the gas may be defined by the equation $f(m, T, V_1) = 0$, and the final state by $f(m, T, V_2) = 0$, the result being that heat has been converted into an equivalent amount of work, but this energy change has been accompanied by a *change in state* of the gas itself.

(b) Isothermal evaporation of a liquid against a pressure less than its vapor pressure.

Again we may define the initial and final states by the equations:

$$f(m_1, m_2, T, V) = 0$$

$$f(m_1 - dm_1, m_2 + dm_2, T, V + dv) = 0$$

Again a change in state is the compensation.

(c) Finally, consider the isothermal production of electricity by means of a voltaic cell. We consider that the electricity is produced as a result of a chemical change, which is itself the summation of the two electrode reactions, the chemical change being accompanied by an evolution of heat or heat is absorbed from the surroundings. Here again we have a simultaneous production of energy from heat and a change in state.

So that, from experience, we may say that an isothermal process can convert heat into work only if that isothermal process be accompanied by a change in state. This may be called conveniently the First Half of the Second Law of Thermodynamics.

Since an isothermal process must be accompanied by a change of state, it follows at once that an isothermal *cycle* cannot convert heat into work.

A cycle involves no change in state. If it were possible by such an isothermal cycle to convert heat into work, we could (to use the classical example) utilize the heat of the ocean and convert this immense reservoir of heat into useful work. The first half of the Second Law says that this is impossible.

Such perpetual motion obtained from an isothermal cycle has been called "perpetual motion of the second kind." Hence, the statement of the Second Law found sometimes: "Perpetual motion of the second kind is impossible."

From the First Half of the Second Law arises also the concept of a reversible process. For example, the expansion of a perfect gas from state A to state B may be carried out in such a way that a definite maximum amount of work can be obtained from it. Now since work cannot be obtained from heat by means of an isothermal cycle, it will require as a *minimum* amount of work to restore the gas from State B to State A, a quantity of work equal to the *maximum* obtained by the expansion. Otherwise, if it were possible to return to the original state by expending a smaller amount of work, the difference would be gained as useful work by means of an isothermal cycle. This is contrary to experience. We define, therefore, a process as reversible if the maximum amount of work is obtained from it, or the minimum is expended on it. Otherwise the process is irreversible, and here again experience has shown that all naturally occurring spontaneous processes are irreversible. Consequently, the work-producing *power* of the universe (as we know it) is continually decreasing; for to restore things to their original state, we would have to expend a *greater* amount of work than can be obtained from the irreversible processes. This is the idea contained in the Principle of the Degradation of Energy, sometimes given as a statement of the Second Law.

Now, since any definite change in state is capable of producing a definite maximum quantity of work, a quantity that is never exceeded no matter what the process be by which the change in state takes place, we may say that a system in a given state possesses a definite capacity for doing work. It has a definite work content, A , and this changes by a definite amount in going from an initial to a final state, where its work content is A_2 . Then $A_1 - A_2$ is the maximum work obtainable by the change in state from state 1 to state 2.

$$A_1 - A_2 = -\Delta A = W_R,$$

where W_R represents the reversible work, and we may write where W represents the work obtained by any process:

$$\begin{array}{ll} W = -\Delta A & \text{for a reversible process} \\ W < -\Delta A & \text{for an irreversible process} \\ W > \Delta A & \text{NEVER} \end{array}$$

So that a mathematical expression for the First Half of the Second Law may be given as $-\Delta A = W_R$.

2. The second case we have to consider is that in which heat is converted into work and is accompanied by *no change in state*, i.e., the case where

we have a cycle, and obviously from the First Half of the Law, this cycle cannot be an isothermal one. What is the compensation, therefore, when heat is converted into work by a cycle which is not isothermal throughout?

Again from experience, we find in this case that always a certain amount of heat may be taken up at a given temperature; a part of this heat may be converted into work, but the remainder of it must be given up at a lower temperature. This rejection at a lower temperature of part of the heat taken up at the higher is the compensation.

This case finds its mathematical expression in the familiar form derived by means of a Carnot or other cycle:

$$\frac{Q_1 - Q_2}{Q_1} = \frac{\Sigma W}{Q_1} = \frac{T_1 - T_2}{T_1}$$

The rejection of the quantity of heat Q_2 at the temperature T_2 is the compensation.

The two halves of the law may be considered together best in the following form:

First Half

An isothermal cycle cannot convert heat into work.

Consider a process in which the working fluid is an ideal gas. Carnot's theorem has shown that the conclusions drawn with an ideal gas as working fluid will hold independently of the material used.

Then for a perfect gas, the change in internal energy is given by:

$$dU = \partial U/\partial T \cdot dT + \partial U/\partial v \cdot dv + \partial U/\partial p \cdot dp.$$

and $\partial U/\partial v = 0$, $\partial U/\partial p = 0$, and \therefore for $dT = 0$, $dU = 0$.

i.e., for an isothermal process.

Now consider an isothermal process I in which a gas expands from A to B.

The First Law says:

$$-\Delta U = -Q_1 + W_1$$

$$-\Delta U = 0$$

$$\therefore Q_1 = W_1$$

and for an isothermal process

Consider the isothermal process II in which the gas is compressed B to A. Again by the First Law:

$$0 = Q_2 - W_2 \text{ or } Q_2 = W_2$$

Then $Q_1 - Q_2 = W_1 - W_2$ by the First Law. Now the Second Law applies and says that $Q_1 - Q_2 = W_1 - W_2 > 0$, i.e., we cannot absorb a quantity of Heat Q_1 at a temperature T_1 , and by reversing the process give up a smaller quantity of heat Q_2 at the temperature T_1 , thereby converting the quantity of heat $Q_1 - Q_2$ into the equivalent quantity of work $W_1 - W_2$ at the constant temperature T_1 , or an isothermal cycle cannot convert heat into work.

$$\text{Again } Q_1 - Q_2 = W_1 - W_2 > 0$$

$$\text{but } Q_1 - Q_2 = W_1 - W_2 \text{ may} = 0$$

and if $W_1 - W_2 = 0$, $W_1 = W_2$ and the process is reversible and $W_1 =$ maximum work done by the system going from A to B; and W_2 is the maximum amount of work that must be done on the system to restore it from B to A.

The Second Half of the Second Law is as follows:

If we allow the expansion A to B to take place isothermally at a higher temperature T_1 again for process 1 at T_1 , $Q_1 = W_1$.

If we consider the process B to A to take place at lower temperature T_2 , for process 2

$$Q_2 = W_2$$

From the First Law as before $Q_1 - Q_2 = W_1 - W_2$ and the Second Law now says $Q_1 - Q_2 = W_1 - W_2$ can be > 0 i.e. Q_1 can be greater than Q_2 , or we can absorb a quantity of heat Q_1 at the higher temperature T_1 , and then reversing the process can give up a smaller quantity of heat Q_2 at the lower temperature T_2 , thereby converting the quantity of heat $Q_1 - Q_2$ into the equivalent quantity of work $W_1 - W_2$.

So far we have been able to correlate several of the expressions for the Second Law with the fundamental statement: Heat cannot be converted into work without compensation. It remains to show now that those expressions involving the ideas of entropy, and of free energy also follow.

The expression $Q_1 - Q_2 = \Sigma W = Q_1 \frac{T_1 - T_2}{T_1}$ has always been derived

by the use of a reversible cycle, and it is shown in elementary books upon Thermodynamics that for a reversible cycle $Q_1/T_1 + Q_2/T_2 = 0$, and that for a cycle in which there is an element of irreversibility $Q_1/T_1 + Q_2/T_2 < 0$. Further it is shown that for any cyclic process involving only reversible elements $\Sigma Q/T = 0$, or for a process consisting of infinitesimal elements $\int Q/T = 0$. Then for a cycle consisting of the change in state A to B by the path A C B followed by change in state B to A by the path B D A, $\int Q/T = 0$.

This may be broken up into the two parts as follows:

$$\int_0 Q/T = \int_A^B \left(\frac{Q}{T}\right)_{ACB} + \int_B^A \left(\frac{Q}{T}\right)_{BDA} = 0$$

i.e.
$$\int_A^B \left(\frac{Q}{T}\right)_{ACB} - \int_A^B \left(\frac{Q}{T}\right)_{BDA} = 0$$

or
$$\int_A^B \left(\frac{Q}{T}\right)_{ACB} = \int_A^B \left(\frac{Q}{T}\right)_{ADB}$$

i.e. the value $\int Q/T$ depends upon the initial and final states alone.

$\therefore \int_A^B Q/T = S_B - S_A$ where S has been called the entropy of the system in the

given state, and dS from the above is seen to be an exact differential. Again it has been stated that for a cycle which involves an element of irreversibility $\sum Q/T < 0$, or $\int Q/T < 0$, i.e. in such a cycle the entropy of the system has decreased.

Suppose now that we have a cyclic process made up of the paths A B C, C D A, where A B C is an *irreversible* change in state, and C D A is a reversible path. Then for the whole cycle $\int Q/T < 0$ and for the path C D A,

$$\int_C^A \frac{Q}{T} = S_A - S_C.$$

For the path A B C.

$$\int_A^C \frac{Q}{T} = \int_C^A \frac{Q}{T} - (S_A - S_C) \text{ and } \int_C^A \frac{Q}{T} < 0$$

$$\therefore \int_A^C \frac{Q}{T} = S_C - S_A - \delta'$$

$$\text{or } \int_A^C \frac{Q}{T} < \Delta S$$

or $Q/T < dS$ i.e. $TdS > Q$ or $TdS = Q + \delta$ where $\delta =$ some positive quantity. Now for an isolated system $Q = 0$ as well as W , i.e. an irreversible change in an isolated system is always accompanied by an increase in entropy. In some way, the system itself generates entropy. This is immediately recognized as another statement of the Second Law.

It may be shown now, quite readily, that the spontaneous transfer of heat from a hotter to a colder body is an irreversible process and as such is accompanied by an increase in entropy. From the fact that this is an irreversible process follows at once the well-known statement of the Second Law; Heat cannot of itself pass from a colder to a hotter body.

The most general expression for the Second Law now becomes $\delta U \geq T\delta S - p\delta V$, where the equality sign applies to reversible changes in an isolated system, and the inequality to irreversible processes; and in addition this equation applies to a system of invariable mass.

Now in the science of chemical thermodynamics, we find ourselves at once at variance with classical thermodynamics, for chemical processes do not occur in isolated systems, but in systems surrounded by a medium (e.g. air, the containing vessel, etc.). It is necessary therefore, to extend the equation $\delta U \geq T\delta S - p\delta V$ before it can be used successfully in chemistry.

Our extension is, that the system plus the surroundings constitute an isolated system. Then if S be the entropy of the system and S_0 that of the surroundings, and if we also assume that all changes in the surroundings take place reversibly, the relation $\delta S + \delta S_0 \geq 0$ holds.

Then if in an infinitesimal stage of a process the heat q is absorbed from the surroundings, from the first law, $\delta U = q - p\delta V$.

Again the increase in entropy of the surroundings $\delta S_0 = -q/T$

$$\therefore \delta S - \frac{q}{T} \geq 0 \text{ or from the equation for the first law. } \delta S - \frac{\delta U + p\delta V}{T} \geq 0$$

or $\delta U \geq T\delta S - p\delta V$, an expression of exactly the same form as we have obtained above for an isolated system.

Now it is quite possible by such devices as the van't Hoff Equilibrium Box and semi-permeable membranes, to bring about our desired changes of state reversibly, so that we may drop the inequality sign and write our first fundamental equation of chemical thermodynamics as

$$\delta U = T\delta S - p\delta V,$$

for a system of invariable mass.

Now the energy of a system may be expressed $U = f(S, V, m_1, m_2, \dots, m_k)$ and for any reversible change in state for which the composition of the system remains invariable

$$\delta U = T\delta S - p\delta V.$$

Now it is possible to change the entropy by the addition or subtraction of heat, the volume may be altered by work done on or by the system, both types of changes producing corresponding changes in energy. It is possible, however, to increase or diminish the energy, entropy and volume of the system simultaneously by increasing or diminishing its mass while the internal physical state as determined by p and T remains the same

Then for a change in mass dm for any one of the components we write

$$\begin{aligned} dU &= \delta V + U_0 dm \\ dS &= \delta S + S_0 dm \\ dV &= \delta V + V_0 dm \end{aligned}$$

and solving for δU , δS , δV and substituting in our original equation $\delta U = T\delta S - p\delta V$ we obtain $dU = TdS - pdV + (U_0 - TS_0 + pV_0) dm$. where U_0 , S_0 , V_0 represent the energy, entropy and volume of unit mass under the specified conditions of temperature and pressure

Now letting $U_0 - TS_0 + pV_0 = \mu$, Gibbs chemical potential for the substance, we have finally

$$dU = TdS - pdV + \mu dm$$

The general equation, then, extended to any number of independently variable components becomes,

$$dU = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \dots + \mu_k dm_k$$

This equation has been of fundamental importance in chemistry because of the variety of forms into which it may be transformed. For example,

$$dU - TdS = -pdV + \mu_1 dm_1 + \mu_2 dm_2 + \dots$$

If T and V are constant

$$dU - TdS = \Sigma \mu dm.$$

or

$$d(U - TS)_{T,V} = \Sigma \mu dm$$

The function $U - TS$ has been called the Free Energy Function, but is known in this country as the work function, or work content A .

$$\begin{aligned} \text{Now} \quad A_1 &= U_1 - TS_1 \\ A_2 &= U_2 - TS_2 \end{aligned}$$

Therefore if by a reversible process we go from state 1 to state 2,

$$\begin{aligned} A_1 - A_2 &= (U_1 - U_2) + T(S_2 - S_1) \\ &= -\Delta U + Q = W_R \end{aligned}$$

a conclusion which we had reached from a fundamental consideration of the Second Law.

Again our fundamental equation may be put into the form.

$$dU - TdS + pdV = \mu_1 dm_1 + \mu_2 dm_2 + \dots$$

For constant temperature and pressure.

$$d(U - TS + pV)_{T,p} = \sum \mu dm$$

and the function $U - TS + pV$ has been known as the thermodynamic potential, but in this country is known as the free energy function F . Since dA and dF are exact differentials, A and F are functions of the state of the system only. This means that $-\Delta A$ and $-\Delta F$ are independent of the path by which the process is carried out. Evidently

$$\begin{aligned} F_1 - F_2 &= -\Delta F = A_1 - A_2 + pV_1 - pV_2 \\ &= -\Delta A - p\Delta V \\ &= W_R - p\Delta V. \end{aligned}$$

Since chemical reactions are regularly carried out at constant temperature and pressure, this function has found ready application in chemistry as will be shown below,

$$\begin{aligned} F_1 &= U_1 + pV_1 - TS_1 \\ F_2 &= U_2 + pV_2 - TS_2 \\ \therefore F_1 - F_2 &= (U_1 - U_2) + p(V_1 - V_2) + T(S_2 - S_1) \\ &= -\Delta U + [T\Delta S - p\Delta V] \\ &= 0 \end{aligned}$$

since $\Delta U = T\Delta S - p\Delta V$ for a finite reversible change at constant temperature and pressure, but for a finite irreversible change at constant temperature and pressure, $T\Delta S - p\Delta V > \Delta U$

$\therefore F_1 - F_2 = \delta$, some positive quantity.

\therefore For an irreversible change $(-\Delta F)_{T,p} > 0$.

And in this we have a criterion for an irreversible or spontaneous process. This is of supreme importance to the chemist for in this quantity $(-\Delta F)_{T,p} > 0$, he has a criterion as to which of his reactions will go, a criterion as to which reactions may possibly be catalyzed, and, more important still, a quantity which will enable him actually to calculate his equilibrium concentrations.

Again he has in this quantity a criterion of physical or chemical equilibrium. For, imagine a system in equilibrium to undergo an infinitesimally small reversible change from equilibrium at constant temperature and pressure,

$$\text{Then} \quad (dF)_{T,p} = 0$$

Again we have seen that

$$U = f(S, V, m_1, m_2, \dots, m_k)$$

$$\text{Then} \quad dU = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \dots$$

$$\text{and} \quad dU = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \frac{\partial U}{\partial m_1} dm_1 + \frac{\partial U}{\partial m_2} dm_2 + \dots$$

$$\text{whence} \quad T = \frac{\partial U}{\partial S}, p = -\frac{\partial U}{\partial V}, \mu_1 = \frac{\partial U}{\partial m_1}, \dots$$

Now U is a homogeneous function of the first degree in $S, V, m_1, m_2, m_3, \dots, m_K$.

\therefore By Euler's Theorem

$$U = S \frac{\partial U}{\partial S} + V \frac{\partial U}{\partial V} + m_1 \frac{\partial U}{\partial m_1} + m_2 \frac{\partial U}{\partial m_2} + \dots$$

and therefore from the relations given above

$$U = TS - pV + \mu_1 m_1 + \mu_2 m_2 + \dots$$

Differentiating

$$dU = TdS + SdT - pdV - Vdp + \mu_1 dm_1$$

$$+ m_1 d\mu_1 + \mu_2 dm_2 + m_2 d\mu_2 + \dots$$

$$\therefore 0 = SdT - vdp + m_1 d\mu_1 + m_2 d\mu_2 + \dots$$

$$\text{Again} \quad F = \mu_1 m_1 + \mu_2 m_2 + \mu_3 m_3 + \dots$$

$$dF = \mu_1 dm_1 + m_1 d\mu_1 + \mu_2 dm_2 + m_2 d\mu_2 + \dots$$

$$\therefore dF = -SdT + vdp + \mu_1 dm_1 + \mu_2 dm_2$$

$$\text{whence} \quad m_1 d\mu_1 + m_2 d\mu_2 + \dots = Vdp - SdT.$$

Collecting our equations involving F , we have,

$$\text{For equilibrium, } (dF)_{T,P} = 0.$$

For a finite reversible change at constant T and p ,

$$-\Delta F = 0$$

For a finite irreversible change at constant T and P

$$-\Delta F > 0$$

$$\text{Again} \quad (dF)_{T,P} = \sum \mu dm.$$

$$\text{and} \quad m_1 d\mu_1 + m_2 d\mu_2 + \dots = Vdp - SdT.$$

By an application to chemistry of these equations, obtained ultimately from the First and Second Laws of thermodynamics, such varied expressions as the following may be derived readily:

The Mass Action Equation, the Phase Rule, the Equations for the Colligative Properties of solutions, the Clapeyron-Clausius Equation, the van't Hoff Isotherm and Isochore; the electromotive forces of voltaic cells, the variation of the equilibrium constant with the temperature, the fugacity and activity relations, etc., etc., and of late years it has been possible to calculate tables of standard Free Energies of Formation (Standard Affinity Tables.)

Thus from the fundamental statement of the Second Law: "Heat cannot be converted into work without compensation," we have led ourselves finally to the familiar laws of physical chemistry and of chemical thermodynamics.

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THE OXYGEN ELECTRODE AS A QUASI-QUANTITATIVE INSTRUMENT*

BY WILLIAM T. RICHARDS

Before 1915 the thermodynamic value of the hydrogen-oxygen chain had been definitely fixed as 1.23 volts by indirect methods¹, and the attempt to obtain reversible potentials with the platinum-oxygen gas electrode had been abandoned. Only recently has interest in this electrode been revived from a more practical point of view, and little or no theoretical discussion has accompanied it. Furman² and Rideal and Goard³ and others⁴ have, however, demonstrated that the instrument is of some practical value.

It is with the hope of extending the range of usefulness of this electrode in analytical work for the determination of hydrogen-ion activities and the partial pressure of oxygen in gaseous mixtures that the present communication is presented. The results given herein are essentially a condensed version of one-fifth of a thesis submitted to the Department of Chemistry of Harvard University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in May 1924, and were for the most part obtained in the Wolcott Gibbs Laboratory under the supervision of Professor T. W. Richards. They were intended to substantiate a theorem which it was found necessary to abandon, and have not been previously published because the writer did not consider them of general interest. No priority is claimed for that part of the work which has been subsequently and much more completely investigated by others. In order to prevent the paper from assuming the proportions of a Gargantua without the vitality of that engaging character, it has been necessary to suppress both a lengthy historical introduction and many numerical data. Any one to whom these may be of use may obtain them either from the files of Harvard University or by personal communication with the author.

References to the literature will be confined only to those most closely touching the work in hand and, to avoid duplication and consequent waste of space, be quoted largely in the final explanatory section. Many which have been necessarily omitted may be found in the papers of Schoch⁵ or Furman.⁶

* Contribution from the Chemical Laboratory of Princeton University.

¹ Nernst and von Wartenberg: *Z. physik. Chem.*, **56**, 534 (1906); *Nachr. kgl. Ges. Wiss., Göttingen*, 1905, 35; Löwenstein: *Z. physik. Chem.*, **54**, 715 (1905); von Wartenberg: *ibid.*, **56**, 513 (1906); Langmuir: *J. Am. Chem. Soc.*, **28**, 1357; Lewis: 139 (1906); Böttger: *Z. physik. Chem.*, **46**, 521 (1903); Noyes and Kohr: **42**, 336 (1903); Brønsted: **65**, 84, 744 (1909); Taylor and Hulet: *J. Phys. Chem.*, **17**, 565 (1913); Lewis: *J. Am. Chem. Soc.*, **28**, 158 (1906); *Z. physik. Chem.*, **53**, 465 (1906).

² Furman: *J. Am. Chem. Soc.*, **44**, 2685 (1922); *Trans. Am. Electrochem. Soc.*, **43**, 79 (1923).

³ Goard and Rideal: *Trans. Faraday Soc.*, **19**, 740 (1924).

⁴ Britton: *J. Chem. Soc.*, 125 1572 (1924); 127, 1896 (1925); 130, 147 (1927); Smith and Giesy: *J. Am. Pharm. Assoc.*, **12**, 855 (1923); Tilley and Ralston: *Trans. Am. Electrochem. Soc.*, **44**, 31 (1923).

⁵ Schoch: *J. Phys. Chem.*, **14**, 665 (1910).

⁶ Furman: *J. Am. Chem. Soc.*, **44**, 2685 (1922); *Trans. Am. Electrochem. Soc.*, **43**, 79 (1923).

1. The Preparation of the Electrode Surface

Although a systematic experimental summary of the conditions affecting potential of the oxygen-platinum electrode have not been made, investigators are unanimous in ascribing great importance in the behaviour of the electrode to factors of preparation and environment. It has been found by the present writer that, for the obtainment of reproducible results, certain details of preparation must be observed; these are briefly enumerated below.

i. The electrode surface should be as large as possible. Whereas the dissociating power of platinum for hydrogen is large, and a small electrode gives reproducible potential values, its dissociating power for oxygen is small, and a very large electrode is advisable. In this investigation electrodes of sheet platinum 1×2 cm. were used. They were heavily coated with platinum black by the usual electrolytic process, using platinum chloride free from lead acetate, a high current density, and an e.m.f. of about 10 volts. They were heated orange red and replatinized when they began to give irregular values due to poisoning.

ii. After platinization and washing, the electrodes were transferred to a dilute oxysalt (preferably borate or phosphate) solution, and alternately made anode and cathode in this solution to remove traces of chloride ion due to the initial plating. A great difference was observed if the electrode was finally made anode or cathode in this process. In the former case, the potential of the oxygen-hydrogen chain may be raised to 1.5 volts when the electrode is subsequently connected to a gas-cell chain, the magnitude of this effect being approximately proportional to the current density and to the length of time of electrolysis. A rise in electrode potential of this kind may appropriately be termed a "superpotential" to indicate that it is consequent upon and the inverse aspect of overvoltage. In electrolyte solutions the superpotential of the oxygen electrode was quickly discharged. If the electrode was dried immediately after the purifying electrolysis it retained, however, its excess charge for many days but not indefinitely. If last made cathode in the purifying electrolysis, the electrode caused the hydrogen-oxygen chain to have a very low initial potential, which quickly rose to a value about 1.0 volts followed by a gradual fall toward the same limit as that approached asymptotically by the over-charged electrode. An electrode which has reached this final, virtually constant, value will be spoken of as a "seasoned" electrode in the subsequent text, and will be used in all measurements, unless otherwise specified, as the only reliable oxygen electrode. "Seasoning" may also be effected, although not as safely, by discontinuing electrolysis, with the electrode as the anode, at the first instant that gas bubbles are seen to appear on its surface with a low current density.

iii. The surface immersed of the platinum electrode must be maintained as constant as possible, a sudden large increase of immersed surface causing a sudden fall in potential. The simplest method of maintaining adequate constancy of this condition is to have a stream of oxygen gas bubbling through the solution sufficient to keep wet the entire surface of the electrode. This

is also made necessary by the fact, brought out in Section 4, that the potential of the electrode is dependent upon the partial pressure of oxygen gas above the solution.

iv. The type of solution in which measurements are made has also a profound effect on the constancy of the oxygen electrode potential. Furman¹ mentions a greater fall per unit time in alkaline than in acid solutions, and earlier investigators have mentioned specifically the effect of sulphate ions.² If, as seems incontestible, the potential of the electrode is due at least in part to an oxide of platinum, the oxidizing power of the medium in which it is immersed should influence its magnitude. This was, indeed, found to be true. Nitrate solutions gave a continual fall in potential, sulfate solutions a somewhat less rapid fall, and only phosphate and borate solutions—both excessively hard to reduce—gave results approaching constancy.

2. Apparatus: A Simple Cell with a Flowing Junction

The Hildebrand type of hydrogen electrode³ showed, in comparative tests, considerably less ability to give quickly a sharp reproducible hydrogen potential than did the enclosed type of electrode where the partial pressure of the gas is maintained constant at one atmosphere over a saturated solution. This type of electrode was therefore abandoned by analogy for oxygen.

An electrode-chain with a flowing junction⁴ using only small portions of solution was devised in its place which, although familiar in principle, is perhaps sufficiently convenient to warrant description. It is pictured in Fig. 1. *A* represents the hydrogen electrode vessel with its bubbling jet. *B* represents a normal calomel electrode of convenient design fitted with a pressure bulb *H* which is level with another pressure bulb *I*, also connected with the chain. *C* and *D* are three-way stopcocks of the *T* type connected with their arms in series, their stems being oppositely directed. The tube *J* serves as an outlet for the dropping bridge. The pressure bulb *I* filled with the solution under measurement in *A*, is level with the potassium chloride pressure bulb *H*. The thermostat level is kept at *TT'* thus immersing at constant temperature all of the apparatus save only the junction stopcocks and tubing. If the room temperature is approximately constant this device assures reproducibility of the junction potential. It is convenient to bend the apparatus normal to the paper at *KK'* thus allowing the outlet tube *J* to drop outside the thermostat into a conveniently placed vessel. The only point at which this apparatus can claim the least originality is at the stopcock *C*. One arm of the bore of this stopcock, that nearest the hydrogen electrode when all three passages are opened, is tightly plugged with absorbent cotton. Thus a clear passage is left between *I* and *D*, but the flow of solution *I* into *A* is effectually prevented, while, at the same time, electrical conduction

¹ Furman: *J. Am. Chem. Soc.*, 44, 2685 (1922); *Trans. Am. Electrochem. Soc.*, 43, 79 (1923).

² Bose: *Z. physik. Chem.*, 38, 1 (1901); *Z. Elektrochemie*, 7, 817 (1901); Wilsmore: *Z. physik. Chem.*, 35, 291 (1900).

³ Hildebrand: *J. Am. Chem. Soc.*, 35, 847 (1913).

⁴ Lamb and Larson: *J. Am. Chem. Soc.*, 42, 229 (1920).

is freely maintained by the saturation of the plug with the solution under measurement. Because of this treatment it is best to use in stopcock *C* a solid bored plug rather than a hollow blown plug.

The procedure in using the apparatus is as follows: After filling the electrode vessels *A* and *B* and the pressure bulbs *I* and *H* with suitable solutions, enough liquid is allowed to run through the tube system, by adjustment of *C* and *D* and the stopcocks controlling the contents of the pressure bulbs, so that a liquid junction is effected at *D*. *D* is then completely

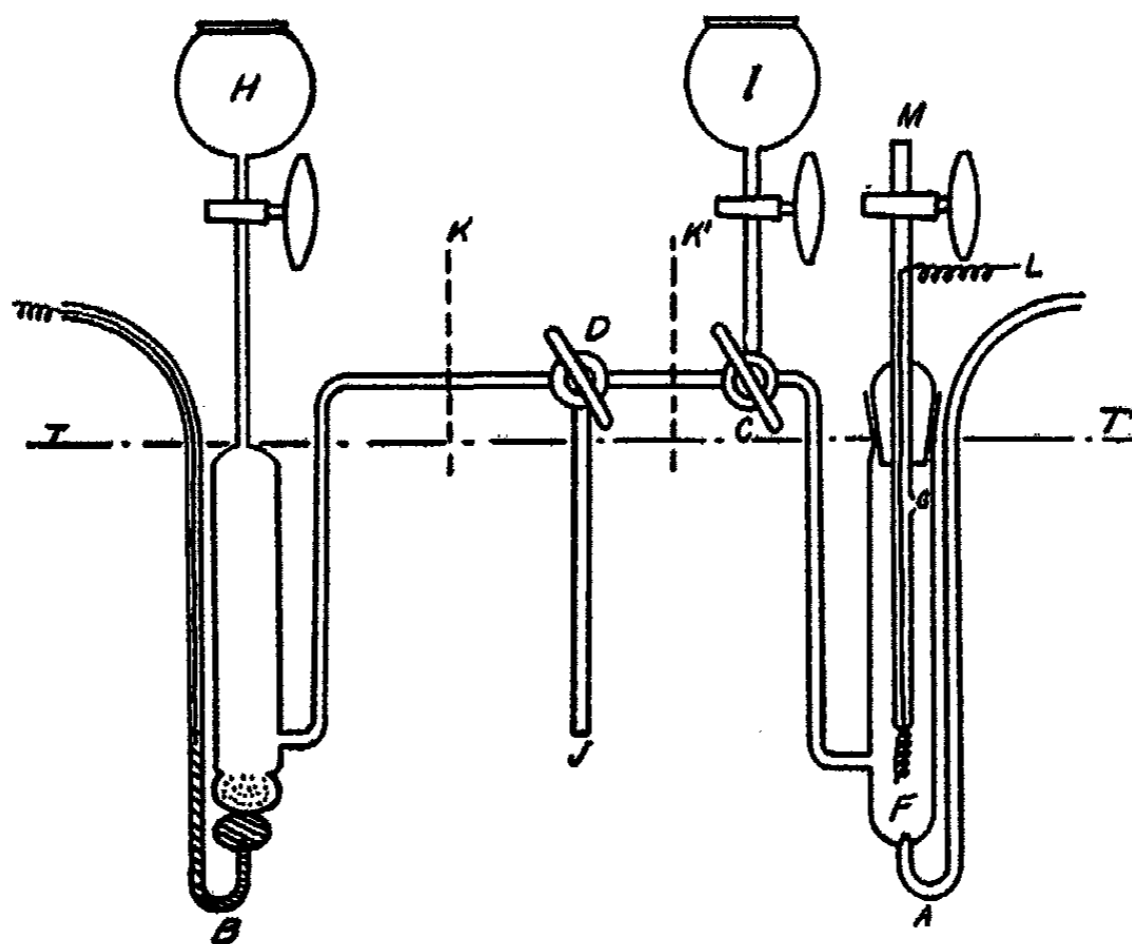


FIG. 1

A calomel-hydrogen cell chain with a flowing junction.

closed and the potential measurements carried out until a satisfactory constancy has been observed. During the time necessary for this process the value of the junction difference has altered, and the total potential of the chain therefore no longer represents its reproducible value. By a suitable adjustment of *D*, and of the pressure bulb stopcocks, a gentle dropping of both liquids is then secured, and a changing liquid junction surface is formed at *D* and removed through *J*. The potentiometer reading is then taken, and its definitive value recorded. If the bulbs *H* and *I* are of 25 cc. capacity several such readings may be taken without refilling.

The performance of this electrode chain has been very satisfactory. Potentials about the neutral point are reproducible within two tenths of a millivolt and, with acid or alkaline solutions of considerable concentration, within, at worst, a millivolt. The error avoided owing to junction potential change is, of course, directly read upon the establishment of the dropping junction, and is almost invariably as large as a millivolt in neutral solutions.

Such an arrangement makes unnecessary a collodion membrane¹ or the glass bulb device recommended by Bovie and Hughes². No difficulty from the diffusion of calomel into the hydrogen vessel was ever experienced. The system has the advantage of the old-fashioned cotton plug junction method of preventing intercirculation of the solutions under measurement, without its intolerable disadvantage of obscuring the junction effect.

The hydrogen electrode used below had the form which is illustrated in Fig. 1. A ground-glass stopper *F* was fitted to *A* which supported the spiral of platinized platinum wire *E* which served as electrode, and provided an

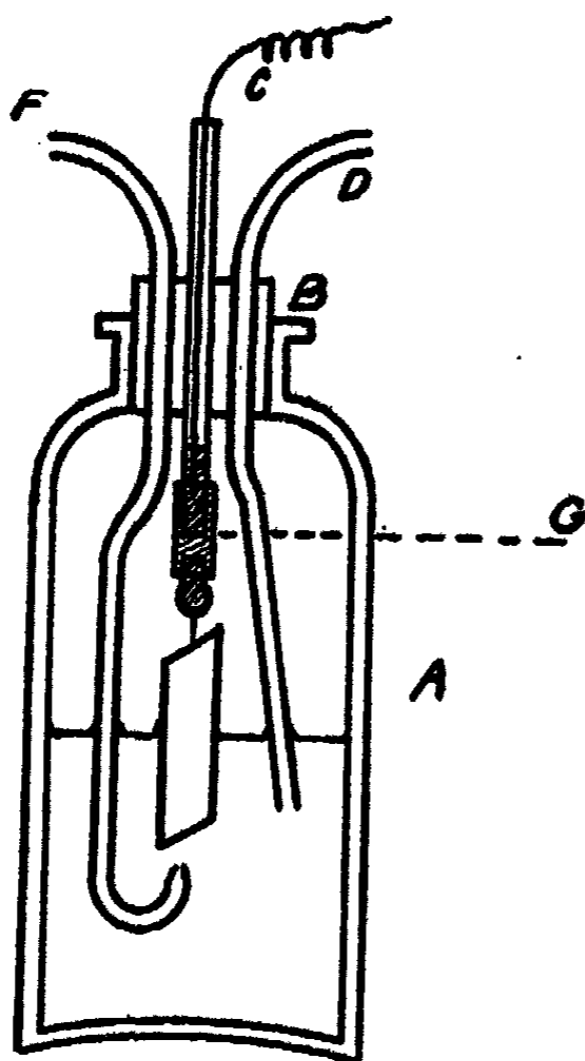


FIG. 2
A convenient form of
oxygen-gas cell.

escaping passage for the bubbled hydrogen gas through *G* and the stopcock *M*. The platinum wire which served as electrode was made continuous from *F* to *L*, being sealed in the glass tube in both places; electrical connection was made by copper wire wrapped around an end left exposed at *L*.

This apparatus was, however, modified for use with the oxygen electrode, both because of the large surface of electrode used, and because a quick change from one solution to another in *A* was often necessary. Hence duplicate bridge systems of the type illustrated in Fig. 1 were constructed which might be alternately connected with *B* by a ground joint at *K'*, the latter being held in place during measurement by rubber bands. The oxygen electrode vessels were of the type illustrated in Fig. 2 where *A* represents a two-ounce wide-mouth bottle. *B* a four-hole rubber stopper (the fourth hole containing an escaping jet for bubbled gas is not shown in the diagram), *C* a centrally

located tube connecting the electrode *E* to the potentiometer by a mercury column in the rubber tube *G* which fits *C* closely, *F* a connection to the stopcock *C* in Fig. 1, and a bubbling jet for maintaining oxygen flow. In this way great flexibility was secured and the advantages of the flowing junction at the same time retained.

A four-finger mercury-toluene regulator was used to control the thermostat temperature within 0.1° of 25.0° . The oxygen used in the cell chain was taken from a compressed cylinder, needing apparently no further purification.

¹ Fales and Stammelman: *J. Am. Chem. Soc.*, 45, 1271 (1923).

² Bovie and Hughes: *J. Am. Chem. Soc.*, 45, 1904 (1923).

Hydrogen was obtained from a battery of four amalgam generators, being purified by Gay-Lussac towers containing 1/10 normal sodium hydroxide and distilled water in the order named. The calomel electrodes in the cell chains were carefully prepared although, in the work below, their constancy and not their absolute value is alone of significance. The potentiometric system was of the usual type, with a sensibility of greater than 0.1 m.v.

3. Constant Oxygen Electrode Potentials

The first step in the standardization of the oxygen electrode is to obtain potentials which, although not reversible in the thermodynamic sense, are at least stable and dependable. Table I indicates that this was accomplished. A single typical determination with a nitrate solution is also appended for comparison. Table I illustrates three effects.

i. That in nitrate solutions there is a perpetual gradual fall in potential which approaches apparently no asymptotic value, and contains none of the "resting points" observed by Lorenz¹ under similar circumstances with a bright platinum electrode.

ii. That constant potentials, of sufficient stability to excuse the conclusion of pioneer workers with the electrode that a reproducible value had been obtained, may readily be established in borate solutions. The existence of a constant but not reversible potential of this kind raises an interesting theoretical point which will be dealt with in Section 6.

TABLE I
Potential of the Oxygen-Hydrogen Chain at 25.0°C in Various Solutions

| No. | Composition | 1 | 2 | 3 | 4 | 5 | 26 days |
|-----|----------------------------------------|-------|-------|-------|-------|-------|---------|
| I | NaNO ₃ , 0.5N | 1.071 | 1.047 | 1.027 | 1.019 | — | 0.965 |
| II | H ₃ BO ₃ , 0.05N | 1.089 | 1.102 | 1.102 | 1.102 | — | — |
| | H ₃ BO ₃ , 0.5N | 1.102 | 1.101 | 1.101 | 1.101 | — | — |
| III | H ₃ BO ₃ , 0.05N | 1.089 | 1.089 | 1.093 | 1.095 | 1.095 | — |
| | H ₃ BO ₃ , 0.5N | 1.087 | 1.088 | 1.088 | 1.088 | — | — |
| IV | H ₃ BO ₃ , 0.05N | 0.981 | 0.999 | 1.001 | 1.001 | 1.001 | — |
| | H ₃ BO ₃ , 0.5N | 0.975 | 0.995 | 0.999 | 0.999 | 0.999 | — |

iii. That, in borate solutions, the average of all values for the concentrated and all for the dilute solutions gives a difference of —.003 volt for the concentrated. This effect is fully investigated and discussed in Section 5.

4. Variation of Potential with Oxygen Pressure

It has been mentioned in Section 1, iii, that the potential of the oxygen electrode is not independent of the partial pressure of the oxygen gas surrounding it. This observation, because of the indication it gives of the nature of the oxygen electrode potential as discussed in Section 6, has been confirmed by a series of measurements summarized in Table II.

¹ Lorenz and Spielmann: Z. Elektrochemie, 15, 293, 349; Lorenz: 661; Lorenz and Lauber: 157, 206 (1909); Spielmann: Trans. Faraday Soc., 5, 88 (1910).

These measurements were obtained with the flowing junction apparatus and carefully seasoned oxygen electrodes which had been brought to constancy of potential with a constant oxygen flow at one atmosphere in a .05 N borax solution. At 0 time an equal flow of nitrogen gas (100 cc. per minute, enough to give vigorous stirring) was turned on by a set of stopcocks which automatically discontinued the oxygen flow: thus the oxygen was gradually swept from the solution with a corresponding fall in potential until the oxygen partial pressure became zero and the nitrogen one atmosphere. At the indicated time the nitrogen flow was discontinued and the oxygen resumed at the same rate of flow; this caused the potential to rise to its former value. The process was quantitatively repeated many times, two characteristic readings only being reproduced. Since, within limit of error of measurement, these two series are congruent, except in the absence of oxygen, they have been indicated graphically in Fig. 3 as a type curve, points from both of the series being set down without distinction.

TABLE II
The Potential of the Oxygen Electrode in the Presence and Absence of Oxygen Gas.

| Determination I | | Determination II | |
|------------------|--------------------------------------------------|------------------|--------------------------------------------------|
| Time (mins) | H ₂ -O ₂ Potential (volts) | Time (mins) | H ₂ -O ₂ Potential (volts) |
| 0 | 0.979 | 0 | 0.979 |
| 1 | 0.970 | 1 | 0.970 |
| 2 | 0.961 | 2 | 0.962 |
| 5 | 0.938 | 5 | 0.938 |
| 12 | 0.898 | 12 | 0.900 |
| 15 | 0.880 | 17 | 0.878 |
| 23 | 0.851 | 28 | 0.838 |
| 38 | 0.811 | 56 | 0.801 |
| 53 | 0.791 | 68 | 0.798 |
| Oxygen turned on | | Oxygen turned on | |
| 0 | 0.790 | 0 | 0.797 |
| 1 | 0.874 | 2 | 0.895 |
| 2 | 0.921 | 3 | 0.937 |
| 3 | 0.942 | 4 | 0.947 |
| 5 | 0.958 | 6 | 0.963 |
| 10 | 0.971 | 8 | 0.969 |
| 15 | 0.978 | 15 | 0.978 |
| 20 | 0.978 | 27 | 0.980 |

At the first 0 time nitrogen was turned on, and oxygen simultaneously discontinued. At the second 0 time the oxygen flow was resumed, and the nitrogen simultaneously discontinued.

They indicate that the oxygen electrode, suitably prepared and standardized, may be used as an analytical instrument in determining the partial pressures of oxygen in a gaseous mixture, an observation which may have a certain application in biology. The effect of increasing the oxygen pressure

above one atmosphere was also investigated, but since a paper by Tammann and Runge¹ has recently appeared treating this matter much more fully the results will not be published. The type of experiment detailed above does not seem to have been attempted by these authors, who were interested chiefly in an attempt to secure the reversible potential of oxygen ions by raising the pressure and temperature.

It should be noted that, at the moment before turning on oxygen gas, although its partial pressure is effectively zero, and although nitrogen is not made electromotively active by platinum, the potential of the oxygen elec-

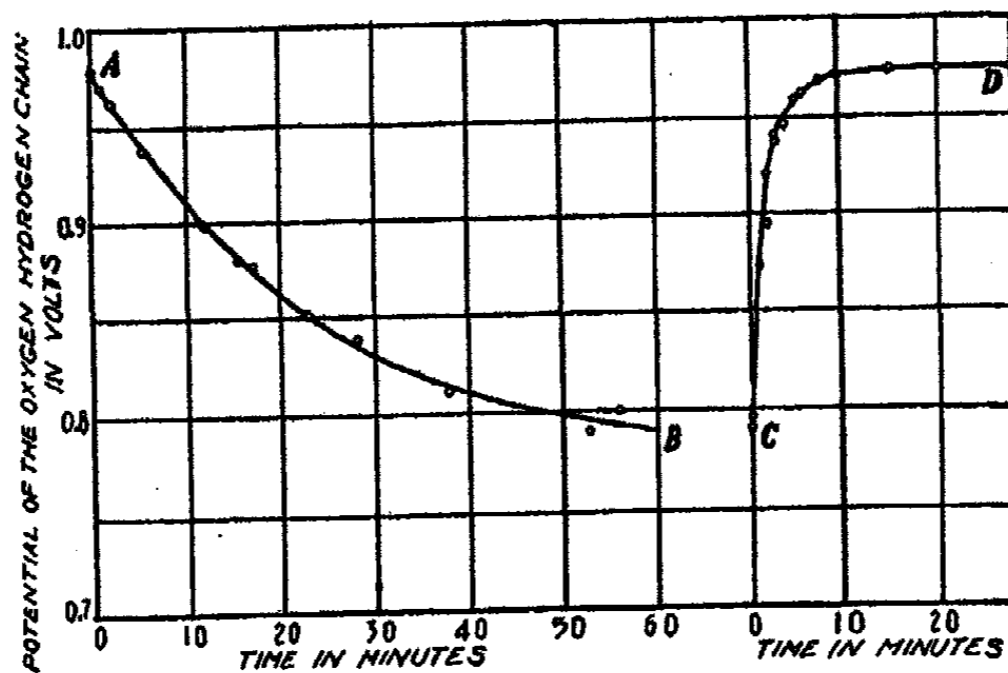


FIG. 3
The variation of the potential of the oxygen electrode with partial pressure of oxygen gas.

At A a current of nitrogen of about 100 cc per minute is turned on, the oxygen flow being simultaneously discontinued. At B all oxygen, with the exception of insignificant traces, has been expelled from the solution. At C the flow of oxygen is resumed, and the nitrogen discontinued. At D the potential of the oxygen electrode is constant at its initial value, and the cycle is repeated.

trode has by no means disappeared but is both finite and constant. This effect may safely be attributed to an irreversible oxidation of the electrode surface. The remaining aspects of the phenomenon are considered in Section 6.

5. The Quantitative Measurement of Hydroxyl Ion Activity

Using the apparatus and experience gained in the preceding sections it was found possible to develop a method of measuring indirectly hydroxyl (and hence hydrogen) ion activity by the oxygen electrode with a precision of a few millivolts. It is possible that Barendrecht² has devised a somewhat similar method but, from his published results, he cannot have worked it out in anything like the detail given below. The method is described at some length in the hope that bio-chemists may find it useful in dealing with oxyhaemoglobin solutions.

¹ G. Tammann and F. Runge: *Z. anorg. allgem. Chem.*, 156, 85 (1927).

² Barendrecht: *Kon. Akad. Wet. Amsterdam*, 22, 2 (1919).

In order to establish the method the following procedure was adopted. Two modifications *A* and *B* of the same solution were adjusted to different hydrogen ion activities by the suitable addition of small quantities of acid. Their hydrogen electrode potentials were then carefully measured at 25° in a thermostat. An oxygen electrode was seasoned in solution *A*, and then removed from the cell (Fig. 2), rinsed with a previously oxygen-saturated portion of solution *B*, and placed in another portion of *B* which had also been oxygen saturated and brought to the temperature of the thermostat. Measurements of potential change with time were then made at suitable intervals for 20 minutes, at the end of which period the potential had almost invariably ceased significant change. The electrode was then removed, rinsed with solution *A* saturated with oxygen, and placed again in the cell chain in a warmed and oxygen-saturated portion of *A*, and the potential again observed for twenty minutes. The process of rinsing, transference, and timed measurement was repeated with both *B* and *A* a second time. Two sets of values were thus obtained for the oxygen electrode potential difference of the two solutions, one by the subtraction of the first resting potential in *A* from the average of the first and second resting potentials in *B*, and the other by the subtraction from the second resting potential in *B* of the average of the first and second resting potentials in *A*. Values obtained in this way are independent of any drift upward or downward resulting from irreversible change of the potential of the oxygen electrode. They express, with a degree of accuracy which is at once an indication of the reliability of the process, the difference in hydroxyl ion activity of the two solutions *A* and *B*. Comparison of the values obtained shows that the increase in oxygen electrode potential is almost exactly equal to the decrease in hydrogen electrode potential in the more acid of the two solutions. On the assumption, surely justifiable, that $[H^+][OH^-] = k$ in any given solution the difference of hydroxyl ion activity between the two solutions may thus be quantitatively measured.

Borate solutions were chosen for most of these tests for obvious reasons, the solutions being 0.05 normal in borate as this concentration is as small as is compatible with the minimum conductivity necessary for the obtainment of accurate potentiometer readings. In order to test the behavior of the electrode in more concentrated solutions a 6 N solution of ammonium sulfate was similarly measured. Somewhat acid solutions were preferably used for two reasons. In the first place, it is much easier, in slightly acid solutions, to obtain invariable hydrogen electrode potentials without careful exclusion of atmospheric carbon dioxide; in the second place, as Furman¹ has pointed out, the oxygen electrode shows greater potential stability in acid solution. A summary of the results obtained is given in Table III. All the measurements are at 25.0° and all potentials are against a normal calomel electrode except, of course, those in columns 6 and 7. In the headings of the columns of this table the symbol π has its usual significance, potential. The table

¹ Furman: *J. Am. Chem. Soc.*, 44, 2685 (1922); *Trans. Am. Electrochem. Soc.*, 43, 79 (1923).

contains all information necessary to calculate the desired quantity, but is in consequence exceedingly condensed. The notation may be expounded by taking a typical case where solutions A and B are under measurement. The electrode, seasoned in A, is transferred to B and observed for twenty minutes. Its potential after two minutes is the first entry in column 1 for the series of measurements in this particular solution. After twenty-one minutes, its potential having become virtually constant, a reading with flowing junction is made and entered in column 5. Solution A is then similarly measured, its oxygen electrode potential after two minutes being the *third* entry in column 1. The second measurement of B after nineteen minutes goes in the second line of column 3, and the second of A on the fourth line. Thus in any given determination from column 1 through column 5 the actual order of the oxygen electrode measurements is first, third, second, fourth, of the values given. The interrupted line subdividing horizontally each determination shows which of the columns gives results applicable to only one of the two solutions, and which gives values common to both. Column 8 gives the alkalinity of the solution.

TABLE III
Measurements of Hydroxyl Ion Activity with the Oxygen Electrode.

| Detn. No. | Column No. Composition | Change of πO with Time, in v. and mins. | | | | | Av. πO differ. | Av. πH differ. | 8 πH |
|-----------|---------------------------|----------------------------------------------|--------|---------|---------|--------------|------------------------|------------------------|--------------|
| | | 1 2 | 2 3 | 3 19 | 4 20 | 5 21 flow | | | |
| 1 | Boric acid— | 0.581 | 0.580 | 0.574 | 0.574 | 0.5745 | | | |
| | Borax, 0.05N | 0.572 | 0.571 | 0.567 | 0.567 | 0.5670 | 0.053 | 0.050 | 0.4943 |
| | Ditto. | 0.622 | 0.623 | 0.624 | 0.624 | 0.6243 | | | |
| | | 0.612 | 0.613 | 0.615 | 0.615 | 0.6163 | | | 0.4446 |
| 2 | Ditto. | 0.496 | 0.496 | 0.496 | 0.496 | 0.4961 | | | |
| | Ditto. | 0.491 | 0.490 | 0.490 | 0.490 | 0.4900 | 0.285 | 0.282 | 0.428 |
| | Ditto. | 0.199 | 0.200 | 0.206 | 0.206 | 0.2057 | | | |
| | Ditto. | 0.197 | 0.198 | 0.211 | 0.211 | 0.2110 | | | 0.703 |
| 3 | Sodium Phosphate, 0.05N | 0.170 | 0.170 | 0.166 | 0.166 | 0.1667 | | | |
| | Boric acid— | 0.154 | 0.156 | 0.189 | 0.190 | 0.1933 | 0.102 | 0.111 | 0.711 |
| | Borax, 0.05N | 0.061 | 0.062 | 0.085 | 0.085 | 0.0855 | | | |
| | Ditto. | 0.075 | 0.076 | 0.082 | 0.082 | 0.0811 | | | 0.822 |
| 4 | Ammonium Sulfate, 5.9N | — | 0.224 | 0.227 | 0.227 | 0.2278 | | | |
| | Ditto. | 0.220 | 0.221 | 0.224 | 0.224 | 0.2258 | 0.233 | 0.241 | 0.624 |
| | Ditto. | 0.454 | 0.454 | 0.459 | 0.459 | 0.4591 | | | |
| | Ditto. | 0.449 | 0.450 | 0.457 | 0.4575 | 0.4575 | | | 0.383 |

The results given in Table III show from a comparison of columns 6 and 7 that in acid solution there is a close quantitative correspondence, both in dilute and concentrated solutions, between the difference of the oxygen

electrode potentials and the difference of the hydrogen potentials of two solutions of different hydrogen ion activity. This indicates that the oxygen electrode in spite of its irreversibility is a reliable measure of relative hydroxyl ion activity.

The procedure in determining the hydroxyl ion activity of an unknown solution is precisely similar except that, of course, the checking hydrogen electrode potential of this solution will not be obtainable. The comparison solution should be adjusted to nearly the same pH, and have approximately the same vapor pressure as the unknown solution. It should preferably contain sodium tetraborate and boric acid in appropriate proportions. The oxygen electrode is seasoned to constancy in this solution, and the procedure above outlined followed. The method of computation of the pH from these results is so obvious and well known that it will not be discussed.

It has been observed in Section 3, iii, that a concentrated solution of borax and boric acid gives a value for the hydrogen-oxygen-chain which is less than that in the dilute solution. Smale¹ found a similar effect, although the solutions in which his measurements were made were never very concentrated. The method just described obviously gives a means of studying this effect rapidly and with considerable accuracy, since it makes long waits for the stable potential to be attained unnecessary and, by eliminating the effect of irreversible change in the potential, brings a greater number of anions into the realm of possible investigation. Only certain concentrated solutions may, however, be so investigated. For example they must not contain as an impurity elements such as lead, arsenic, or antimony, which are capable of poisoning the platinum electrode surface; probably all metals less electro-positive than hydrogen should for this reason be excluded.

Because of their oxidizability, solutions of the alkali halides are obviously unsuitable since, as was pointed out by Lewis,² the halide ion would be oxidized until its potential against free halogen was equal to that of the oxygen electrode. Nitrates, on the other hand, although reduced catalytically by hydrogen electrode, may be made to give satisfactory results by extrapolating to find the initial potential of the hydrogen electrode; a method which has been carefully justified both theoretically and practically. A similar reduction of considerably less importance is observed in concentrated solutions of sodium acetate; it may be dealt with in similar fashion. Solutions of alkali perchlorates, were also found suitable if the sodium chloride normal electrode was substituted for the potassium. Sulfate solutions, after many preliminary tests, were found most suitable of all for this purpose, and were therefore given most attention. Table IV, while not as detailed as its immediate predecessor, gives a summary of the results obtained, and should be self-explanatory.

¹ Smale: *Z. physik. Chem.*, 14, 577 (1894).

² Lewis: *J. Am. Chem. Soc.*, 28, 158 (1906); *Z. physik. Chem.*, 55, 465 (1906).

TABLE IV
The Effect of Increasing Electrolyte Concentration on the Potential of the Hydrogen-Oxygen Chain

| Detn. No. | Composition of Solution | | Average Corrected Oxygen Potential | Hydrogen electrode Potential | Hydrogen Oxygen Chain, volts | Difference between Dilute and Concentrated, volts |
|-----------|-------------------------------------------------|-------|------------------------------------|------------------------------|------------------------------|---------------------------------------------------|
| 1 | H ₃ BO ₃ | 0.5N | 0.208 | 0.719 | 0.927 | 0.008 |
| | H ₃ BO ₃ | 0.05N | .214 | .721 | .935 | |
| 2 | Li ₂ SO ₄ | 0.53N | .498 | .402 | .900 | 0.016 |
| | H ₃ BO ₃ | 0.05N | .510 | .406 | .916 | |
| 3 | K ₂ SO ₄ | 1.2N | .498 | .431 | .920 | 0.025 |
| | H ₃ BO ₃ | 0.05N | .516 | .429 | .945 | |
| 4 | K ₂ SO ₄ | 1.2N | .505 | .431 | .936 | 0.023 |
| | H ₃ BO ₃ | 0.05N | .465 | .494 | .957 | |
| 5 | Li ₂ SO ₄ | 5.3N | .429 | .409 | .838 | 0.092 |
| | H ₃ BO ₃ | 0.05N | .517 | .413 | .930 | |
| 6 | Li ₂ SO ₄ | 5.3N | .458 | .393 | .851 | 0.080 |
| | H ₃ BO ₃ | 0.05N | .344 | .587 | .931 | |
| 7 | (NH ₄) ₂ SO ₄ | 5.9N | .458 | .383 | .841 | 0.067 |
| | H ₃ BO ₃ | 0.05N | .502 | .406 | .908 | |
| 8 | NaClO ₄ | 6.1N | -0.116 | .931 | .815 | 0.081 |
| | H ₃ BO ₃ | 0.05N | -0.038 | .934 | .896 | |
| 9 | NaNO ₃ | 7.5N | .137 | .623 | .760 | 0.146 |
| | Na ₂ HPO ₄ | 0.05N | .282 | .624 | .906 | |

6. Discussion

The theory of the oxygen electrode at present accepted is that its irreversibility is due to a coating of oxide of variable and uncertain composition. With this conclusion the present communication can find no fault. Many writers believe, however, that the measured potential of the electrode is entirely oxidic. This conception originated with Lorenz,¹ was declared final by Schoch,² and has apparently been whole-heartedly accepted in the more recent work by Foerster,³ Grube,⁴ and even Tammann and Runge.⁵ While

¹ Lorenz and Spielmann: *Z. Elektrochemie*, 15, 293, 349 (1909); Spielmann: *Trans. Faraday Soc.*, 5, 88 (1910); Lorenz: *Z. Elektrochemie*, 15, 661; Lorenz and Lauber: 157, 206 (1909).

² Schoch: *J. Phys. Chem.*, 14, 665 (1910).

³ Foerster: *Z. physik. Chem.*, 69, 236 (1909).

⁴ Grube: *Z. Elektrochemie*, 16, 621 (1910).

⁵ G. Tammann and F. Runge: *Z. anorg. allgem. Chem.*, 156, 85 (1927).

the measurements set forth above are by no means a complete refutation of this hypothesis, they furnish evidence which, in conjunction with the work of others, makes it seem highly probable that the electromotive activity of oxygen gas itself, at the platinized surface of the electrode, plays a considerable part in the total effect. A number of phenomena emphasized above are difficult or even impossible to explain on the totally oxidic theory.

The first of these is the superpotential, or high residual voltage after anodic treatment, of the electrode mentioned in Section 1, ii. If this is considered due to a higher unstable oxide of platinum it must, owing to the character of its over-voltage phenomena, be soluble in the electrode in all proportions and decompose according to the law of a monomolecular reaction, a combination of conditions which has few analogies in polyvalent oxidations. Moreover the oxide PtO_4 is necessary to account for the potential of 1.9 volts observed by Foerster for the hydrogen-oxygen chain, since Grube has found the potential of PtO_2 to be only 1.5 volts. PtO_4 , by analogy with RuO_3 and RuO_4 , should be considerably more stable than PtO_2 , whereas it is generally agreed that the superpotential of the electrode is increasingly unstable with increasing magnitude, the function being, in fact, an exponential one. If, on the other hand, it is considered that oxygen gas dissolved in the electrode is responsible for its temporarily elevated potential no similar difficulty is encountered. Although never, apparently, specifically enunciated in this connection, Bose¹ has evidently assumed a similar hypothesis, and the measurements of Harding and Smith² make such a conclusion almost incontestible. These authors, in a paper the importance of which from this point of view can hardly be overestimated, have proved that the electrical resistance of a palladium wire decreases suddenly on being made cathode in electrolysis due to the occlusion of hydrogen. An exactly similar decrease is observed when the wire is made anode, differing only in magnitude from that observed during cathodization, and followed, after the discontinuance of the electrolysing current, by a permanent increase of resistance due to oxide formation.³ Hydrogen occluded under these conditions is generally accepted as being uncombined.³ The extension to oxygen by analogy, and hence to the phenomenon of the superpotential seems at present, therefore, incontestible in view of the feeble character of the opposing evidence. Here, therefore, is a case in which it seems wise to attribute to oxygen gas at least a part of the total electromotive activity.

It may perhaps be brought out, in passing, that no cogent reason is at hand for the belief that oxygen and not hydroxyl ions are crowded into the electrode by the high current density; while unconventional this view is not entirely fantastic.

¹ Bose: *Z. Elektrochemie*, 7, 673 (1901); *Zeit. anorg. Chem.*, 30, 406 (1902).

² Cf. Smith and others: *J. Am. Chem. Soc.*, 38, 2577 (1916); 40, 1508 (1918).

³ T. W. Richards and W. T. Richards: *J. Am. Chem. Soc.*, 46, 89 (1924).

It is difficult also to understand, without attributing electromotive activity to oxygen gas, the often observed phenomenon that an electrode which has not been made anode at once assumes, in the presence of vigorously bubbling oxygen, a potential comparable to that of seasoned anodized electrode under the same conditions. In other words the superpotential and possible oxide formation produced by anodic treatment have no necessary part in the almost instantaneous production of a potential of like magnitude by platinum and oxygen gas alone. Moreover, the quantitative and immediate response of the electrode to variations in the partial pressure of oxygen gas brought out in Section 4 make necessary according to the oxidic theory the reversible formation of high oxides of platinum which Woehler,¹ working under much more favorable conditions, has shown to be formed only during many days.

It may be mentioned in passing that an attempt was made in this connection to measure directly the ionization of oxygen gas due to its passage over a large quantity of platinized asbestos. A specially constructed and very sensitive radioactive electroscopes was used for this purpose. While the ions so produced would have had to traverse a space of only 2 cm. in about one second not the slightest ionization was detected. The failure of this measurement, while disappointing, has obviously no disqualifying effect upon the argument set forth above.

In view of these considerations there seems no valid reason for denying a certain electromotive activity to oxygen gas. That oxide formation is also a factor is hardly contestible, especially in view of the measurements recorded in Section 4. We are then forced to picture the measured potential as a compromise between a low oxidic potential and the only partially attained O_2-2O^- potential. Although theoretically the highest of the several possible potentials in a concentration-chain should alone be manifest, actually a number of such "compromise potentials" are known. For example the half-cells $Fe/FeSO_4, Fe_2(SO_4)_3$; $Pt.H_2/FeSO_4, Fe_2(SO_4)_3$; and $Fe/FeSO_4, H_2SO_4$ have been shown to exhibit a similar effect.² The writer intends, in the near future, to discuss a number of these potentials from the point of view of the velocities of the concomitant reactions involved. Failing such quantitative justification the conception of the "compromise potential" must be accepted as the only solution, however disagreeable, for the situation in hand.

This hypothesis of duality being granted only one further assumption is necessary to account for all apparently anomalous effects which are at hand, namely, that with increasing oxidation of the blacked platinum surface its activating power for oxygen is diminished. This assumption cannot be substantiated by any direct evidence, but seems in itself highly probable, and is in accord with many observations.

For example it was observed that an electrode which had given a stable potential in a solution gave, after having been treated electrolytically only

¹ Woehler: Ber., 36, 3475 (1903).

² T. W. Richards and W. T. Richards: J. Am. Chem. Soc., 46, 89 (1924).

as cathode in boric acid, a potential considerably above its former value in the same solution. There can be very little question from the measurements of Harding and Smith that a film of oxide undergoes reduction upon cathodization. The rise in potential is simply accounted for by the increased electromotive activity of oxygen gas due to a removal of obstructing oxide from the platinum surface. Again, the constancy of potentials in borate solutions noted in Section 2 is made plausible by this explanation. Since both an oxide of platinum and electromotive oxygen gas may reasonably be supposed to be together responsible for the oxygen electrode potential, it does not seem excessively fantastic to suppose that a balance may be reached between the formation of oxide, which is irreversible and in the nature of a poisoning, and the activation of oxygen gas. Since both these processes are weak it might be expected that, with a solution of sufficiently inactive constituents, a metastable balance between the two would ultimately result which would be manifested by constancy of the potential. Any extremely stable solution should give similar results and, in fact, observations of a similar character were made in less investigated but comparable phosphate solutions, whereas in nitrate solutions, where the lowering of the potential due to oxide formation should be much greater, no constancy was observed.

One further phenomenon is elucidated by this interpretation of the oxygen electrode potential, namely, the lowering of the value for the oxygen-hydrogen chain with increasing electrolyte concentration emphasized in Section 5. Several hypotheses may at once be abandoned for this purpose. It is evident that neither a decrease in the ion product of water nor in the activity of dissolved oxygen can be responsible for this result, since both of these values are differently defined thermodynamically. Passivity and poisoning of the oxygen electrode manifest themselves irreversibly and in a very different manner from that observed, and both may be unequivocally discarded as explanations. It has, however, been found convenient to infer a considerable dependence of the dissociating power of platinum black for oxygen on the condition of the platinum surface. With increasing oxysalt concentration an increased oxidation of the surface, with a concomitant loss of dissociating power for oxygen, and a consequent temporary fall in potential is to be expected. It is possible, as an alternate hypothesis to account for this effect, that the hydration of the ions in the concentrated solutions would alone be sufficient. Data are not at hand to treat the matter conclusively.

It is hardly necessary, although agreeable, to acknowledge indebtedness to Professor Theodore W. Richards for his interest in this investigation. To Professor F. G. Donnan of University College, London, the most cordial thanks are also extended for his hospitality under unusual circumstances.

Summary

1. The preparation of an oxygen-platinum electrode capable of giving reproducible results is discussed.
2. A convenient cell chain having a flowing junction and requiring only small volumes of liquid is described.

3. It has been demonstrated that, under suitable conditions, oxygen-electrode potentials constant to a millivolt for many days may be obtained, although these are far below the thermodynamic value for the oxygen-hydrogen chain.

4. The potential of the oxygen electrode has been shown to vary quantitatively but not thermodynamically with the partial pressure of oxygen gas between 0 and 1 atmosphere.

5. A method is described for measuring hydroxyl ion activities with the oxygen electrode which is capable of considerable accuracy.

6. In order to explain these and other phenomena it has been necessary to attribute electromotive activity to oxygen gas, and to consider the measured potential of the electrode a compromise between this and the oxidic potential which is currently believed to produce the total effect.

It is hoped that these findings will prove useful in biochemical work.

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THE ELECTRODYNAMICS OF SURFACE CATALYSIS*

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Perhaps no phase of chemistry has received a more intensive study than has surface catalysis, especially during the past few years. A great mass of evidence has been accumulated which indicates in a most satisfactory manner that a catalytic surface is not uniformly active, but that its ability to promote chemical action seems largely confined to the molecules of gas adsorbed at certain centers or active points on the surface. While this must be looked upon as a decided step in advance, the fundamental mechanism employed by these active centers in promoting chemical action is still an unsolved question.

The writer while investigating the physical side of the reaction process, namely studying the ionic emission during chemical action and the effect of gases on thermionic emission and on contact difference of potential, has been led to certain conclusions that he hopes will add to our knowledge of the reaction process.

The basic principles involved in the proposed mechanism are not fundamentally different from those suggested by Sir J. J. Thomson¹. In brief the mechanism is that the image and intrinsic surface forces combined with kinetic energy of agitation dissociate the gas molecules on the surface into ions; the ions thus formed are driven from the surface by kinetic agitation with a probability distribution of velocities; and that chemical action results from a rearranged combination of the ions thus driven from the surface. In this manner it is possible to treat chemical action as a special case of thermionic emission.

The experimental work, consisting of a study of ionization in reacting gases, and the thermionic emission in the presence of various gases, on which the proposed mechanism is based, has been presented in a series of recent articles^{2,3,4,5,6,7}.

The salient points may be summarized as follows:

1. The ionization, which has been detected in every reaction investigated, is specific for each reaction.
2. The current through the reacting gas is proportional to the number of molecules reacting, but the ratio of ions capable of being removed from

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¹ Sir J. J. Thomson: "The Electron in Chemistry," Chapter IV.

² Trans. Am. Electrochem. Soc., 44, 257 (1923).

³ J. Am. Chem. Soc., 46, 1403 (1924).

⁴ Proc. Nat. Acad., 11, 512 (1925).

⁵ Phys. Rev., 26, 633 (1925).

⁶ Proc. Nat. Acad., 12, 560 (1926).

⁷ Proc. Nat. Acad., 13, 594 (1927).

the reacting gas by an applied voltage to molecules reacting is exceedingly small, being of the order of magnitude of 1 to 10^{12} .

3. The ions present in a surface-catalyzed reaction, such as the oxidation of ethyl alcohol, are liberated only at the electrode surface^{2,4} where the reaction is taking place, with no detectable ionization occurring in the gas volume. Gas phase ionization was observed during the thermal decomposition of ozone, and doubtless exists during the decomposition of nitrogen pentoxide, although the test was not made in the latter case.

4. The ionization current, as well as the amount of chemical action, is dependent on the chemical nature of the surface.^{2,3,4} Platinum and gold gave quite similar results in the cases tested, but copper, iron, brass, glass, copper oxide, iron oxide, and aluminum oxide possessed characteristic properties.

5. The emission during the oxidation of ethyl alcohol and hydrogen on gold and iron and copper oxides, when compared to the thermionic emission from these electrodes in the presence of the gases separately has shown definitely that the ions emitted in the reaction are the same as those emitted thermally. Apparently the chemical action allows ions to escape from the surface at a lower temperature and with less work than when in the presence of the various gases taken singly; this lowering of the temperature and work of emission is more pronounced for the negative than for the positive ions in the case of the oxidation reactions studied.^{5,6,7}

6. The ionization current at atmospheric pressures is directly proportional to the applied difference of potential between the electrodes, i.e., Ohm's Law holds.^{2,3,4,5} This fact seemed surprising until the chemical emission was shown to be a type of thermionic emission where saturation is obtained only at low pressures. The effect of pressure on the saturation current has been given in a series of experiments by Brotherton.⁸ Saturation disappears at pressures as low as a fraction of a millimeter of mercury.

7. The temperature-current curves follow the Richardson equation⁹ for thermionic emission ($i = AT^2 e^{-b/T}$). A straight line is obtained by plotting ($\log i - 1/2 \log T$) against $(1/T \cdot 2.303)$, where b , a measure of the work necessary for the removal of an ion from the surface, is given by the slope of the line.^{4,7}

8. In the case of both thermionic and chemical emissions a definite interdependent relationship was shown to exist between the temperature and work of emission for the positive and negative ions in various gases and reactions.^{7,6} This interdependence has been made use of to postulate the presence of a selective intrinsic force, electrical in nature, existing at the emitting surface. This intrinsic force, it is believed, is one of the controlling factors in thermionic emission in gases, and in chemical action; it is effective to approximately 3×10^{-8} cm. from the surface.

⁸ Brotherton: Proc. Roy. Soc., 105, 468 (1924).

⁹ O. W. Richardson: "The Emission of Electricity from Hot Bodies."

Analysis of Results

While the above phenomena do not offer a direct explanation of the relationship existing between chemical action and ionic emission, yet when the results are analyzed from the standpoint of electrostatics it becomes possible to draw certain definite conclusions regarding the conditions existing on hot surfaces.

Application of the Concept of Electrostatic Image Attraction

Since the ions liberated by the various chemical actions had their origin at the electrodes, they must be treated as charged bodies near a conducting surface. (Little if anything being known about the conditions under which gas phase reactions take place, the discussion will be confined at present to pure surface reactions.) A charged body, situated near a plane conducting surface, will induce a charge in the surface, such that the body will be attracted to the surface by a force equal to that which would be exerted by another charged body of equal but opposite sign, placed at a similar distance behind the surface, that is, at the mirror image of the body in the conductor.

The force of attraction acting on a charge q e.s.u. at a distance r cm from a conducting plane is given by $q^2/4r^2$ dynes. The charge q is in an electric field of $300 q/4r^2$ volts per cm. If q is the electronic charge 4.774×10^{-10} e.s.u., the field acting on a singly charged ion at different distances from the surface is given in the following table.

| Distance from surface in cm. | Volts per cm. | Distance from surface in cm. | Volts per cm. |
|------------------------------|-------------------|------------------------------|-------------------|
| 10^{-4} | 3.6 | 10^{-6} | 3.6×10^4 |
| 10^{-5} | 3.6×10^2 | 10^{-7} | 3.6×10^6 |

It will be noted that a difference of potential between the electrodes of 1000 volts per cm. will just hold in balance an ion situated at 6×10^{-6} cm from the surface. From this it becomes obvious that to remove all the ions from the surface a fall of potential between the electrodes would be required that is far above the break-down potential of the gas; saturation is, therefore, quite impossible for any appreciable gas pressures. It will be noted that the distance a given applied voltage is able to plumb down into the image layer and remove an ion varies with the inverse square root of the voltage.

An important deduction to be drawn from the application of the electrostatic image concept to the straight line relationship existing between current and applied voltages is that the concentration of the ions upon approaching the surface *increases as the inverse cube of the distance*. These calculations, however, take account of only the image force. The recent experiments on the intrinsic force would lead one to believe that a still more rapid increase exists very near the surface. Thus, while these considerations throw no light on what is happening at the surface they do show the condition existing at a very short distance from the surface, in which region it is believed that the ionic rearrangement resulting in chemical action takes place.

The enormous magnitude of the image field would make it seem unlikely that any appreciable change in the amount or rate of reaction could be occasioned by the application of any voltage under the break-down potential of the gas. The question, however, might well repay investigation as there is a possibility of detecting such a change especially in reactions possessing a high chemical work function.

Application of the Richardson Equation.

The straight line relation between voltage and current has made possible the exploration of only the outer region of the image layer (10^{-4} cm) from the surface. The fact that the temperature-current curves follow an equation of the Richardson type, the development of which is presented later, enables the study to be carried much deeper into the surface region.

In the Richardson equation, $i = AT^3e^{-b/T}$, where i is the current per sq. cm. of surface, A and b are constants, and T the absolute temperature, b may be looked upon as a measure of the total work done in removing an ion from some point near the surface to a point outside the sphere of image attraction. This work is $w = bk$, where k is Boltzmann's constant. If we substitute dC/dt for i , and E for w , we have the usual expression for the rate of chemical action. It is significant to note that not only is the form of the equation the same, but that the values of the constants are of the same order of magnitude for chemical action as for thermionic emission in gases; in general b is from two to four times larger than E/k . This close analogy has led some physicists to conclude that thermionic emission is due to chemical action between the emitter and the gas present; Richardson⁹, however, has shown that this cannot be the case, since b is larger than could possibly be expected from a chemical process. Conversely, the fact that b is larger than E/k is in line with the proposed concept that chemical action is a special case of thermionic emission. Thus, for chemical actions, b becomes a measure of the work done in removing an ion, not through the entire image layer, but to a point just far enough from the surface for successful recombination to take place.

The escape of an ion from a surface against its electrostatic image attraction should not be affected by the sign of the charge on the ion, since the image force is purely non-selective in character. A comparison of the values of db and dT for the positive and negative thermionic emission in various gases⁷ has shown that a selective force also exists at the surface. This force is of such a nature that it allows a more ready escape of positive ions from the metals gold, iron, copper, and platinum, but of the negative ions from iron and copper oxides. The nature of this selective force thus imposed on the image force, as given by its behavior, is that of one possessing the properties of a resultant electrical field effective to a few molecular diameters out from the surface. Such a field would be positive for iron and negative for iron oxide, for instance. It has been suggested⁸ that the positive intrinsic field may result from a leakage of the positive field of the nucleus through the electron lattice of the surface atoms (especially those of small atomic

radii), while the diminution and change of sign of the field accompanying the accumulation of oxide on the surface may result from the surface being covered with the negative oxygen ions of the oxide, which, with increasing concentration on the surface, gradually neutralize the positive intrinsic field of the pure metal, and finally, upon high oxidation, actually establish a negative field.⁷ This intrinsic force, which it is believed is one of the controlling factors in thermionic emission, and chemical action, is doubtless very closely allied to contact difference of potential.

Mechanism of Ionization

The thermionic and chemical emission data clearly indicate the presence of positive and negative ions in the image region of an emitting surface, also that the concentration of these ions increases very rapidly upon approaching the surface. While the exact process of ion formation cannot be told with certainty, it is possible that the mechanism is not fundamentally different from that found in solutions, i.e., the molecules of gas are dissociated by the electrical forces at the surface as are the molecules of the solute dissociated by the dielectric forces of the solvent.¹

The strength of the image field in volts capable of drawing an ion to the surface has already been pointed out. This same force will also act, but to a lesser extent, on a neutral molecule having an electrical moment. As the molecule is drawn to the surface, its poles will become more widely separated and just to the extent that the moment is increased, the more strongly will it be drawn to the surface; the forces of attraction and dissociation are, therefore, cumulative.

The image force existing between a molecule of gas and a surface does not become comparable with the binding force in a molecule until the molecule is within about its diameter from the surface. At this point, as has been mentioned, the molecule is also operated on by the intrinsic force tending to draw one ion to the surface and to repel the other outside the region of intrinsic attraction. For metals such as gold, where the intrinsic field is positive in character, the negative ion is held more closely to the surface, while the opposite should be true for a highly oxidized iron surface.

Nature of the Ions

Very little can be told at present about the exact nature of the ions emitted thermally in the presence of single or reacting gases. The negative ion emission in gases on such surfaces as gold and platinum takes place at several hundred degrees lower temperature than does a corresponding electron emission in a vacuum; positive ion emission completely or almost completely disappears in a vacuum while in the presence of a gas it occurs at even lower temperatures than does the negative.

Unfortunately it does not seem likely that mass spectrograph or mobility measurements will be of much help in determining the chemical nature of the ions emitted in the presence of gases, due to the shortness of the mean free path and the association of the ions.

Two general theories have been advanced regarding the nature of the emitted ions. H. A. Wilson¹⁰ has suggested that the positive ions come from the gas through a dissociation of the molecules of gas into positive ions and electrons; the negative ions, on the other hand, he considers to be electrons which are able to escape from the electrode because of an electrical double layer formed by the gas on the surface. The writer has put forward the hypothesis⁷ that the gas molecules are dissociated into positive and negative ions on the surface and hence are atomic in character; this, of course, applies only to those ions emitted in the presence of gases at temperatures below which electron emission would be obtained in a vacuum. In line with this contention, some indirect evidence has been obtained which indicates that ethyl alcohol dissociates into H^+ and $C_2H_5O^-$ ions. It is possible that molecules with small electrical moments dissociate into positive ions and electrons while it seems probable that highly polar molecules are dissociated into positive and negative ions.

Mechanism of Reaction

In order that an ion be able to escape from a surface, it must possess kinetic energy of agitation with a velocity component perpendicular to the surface capable of removing it against the attractive forces to a distance greater than 10^{-4} cm. from the surface; then it becomes a thermion. However, should an ion whose velocity component is less than this come in contact with another ion of opposite charge to form a neutral molecule, the energy necessary to complete the escape becomes materially smaller. If heat is liberated as a result of the union, then the probability of escape is greatly enhanced because of the increased kinetic agitation. However, should such a new born molecule be formed within less than a certain critical distance from the surface, the chance for its escape is small, because in case the surface force is large the probability of being drawn back to the surface and redissociated is proportionately large. It follows, therefore, that the formation of molecules takes place at a point in the image region so far removed from the surface that the chance for redissociation is small.

The energy that an ion must possess in order to move out to this critical distance where it can undergo successful combination is given directly by the equation derived later. The order of magnitude of this energy is approximately half that necessary for the escape of thermions.

While definite evidence is lacking, it does not seem necessary for two gases to react chemically that both be equally dissociated at the surface. In the case of the oxidation of ethyl alcohol, for instance, it was very evident that the ions escaping from the surface region came primarily from the alcohol and not from the oxygen. It is possible that the effect of the partial pressure of the various reactants on the rate of reaction is determined by the degree of dissociation of the respective gases.

¹⁰ H. A. Wilson: *Phil. Trans.*, 208A, 248 (1908).

A Mathematical Analysis of the Reaction Mechanism

The suggested mechanism making surface catalysis a special case of thermionic emission is readily amenable to a mathematical treatment, since it employs only the electrical forces of the surface and the kinetic energy of agitation of the gas.

The analysis should not only be simpler but more elucidating if the various contributing factors are treated individually. Let us consider a plane metal conductor bathed in a gas, and having its surface covered with a melee of gas ions as has been previously outlined. Let the case be simplified, for the present, by assuming no intrinsic force at the surface; the escape of the ions from the conductor is impeded only by their image attractions. Since the image force and the kinetic energy of agitation will be the same for the positive as for the negative ions, the treatment will apply equally well to either.

From the standpoint of the mechanism outlined, the number of molecules of the reaction product formed per second in a given unit volume situated at a distance r from the surface will be a function of the number of ions that it contains.

To determine the rate of escape of the ions from the surface to a region where chemical action is possible, we must consider the velocity distribution of the ions at the surface. The number of ions per unit volume with velocity components between $u + du$, $v + dv$, $w + dw$, is:¹¹

$$dn = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2} \frac{u^2 + v^2 + w^2}{kT}} du dv dw$$

n being the number of ions per unit volume. The number of ions per unit volume having velocity components w_0 to ∞ perpendicular to the surface and any velocity parallel to the surface is:

$$\begin{aligned} N &= n \left(\frac{m}{2\pi kT} \right)^{3/2} \int_{-\infty}^{\infty} e^{-\frac{m u^2}{2kT}} du \int_{-\infty}^{\infty} e^{-\frac{m v^2}{2kT}} dv \int_{w_0}^{\infty} e^{-\frac{m w^2}{2kT}} w dw \\ &= n \sqrt{\frac{kT}{2\pi m}} e^{-\frac{m w_0^2}{2kT}} = n \sqrt{\frac{kT}{2\pi m}} e^{-\frac{\phi}{kT}} \end{aligned}$$

For an ion to be emitted thermally, it must possess energy sufficient to be completely removed from the image layer. However, an ion does not have to possess energy sufficient to make its escape through the image layer to be able to combine with another ion to form a neutral molecule giving chemical action, so w_0 for chemical action is less than w_0 for thermionic emission.

Effect due to the Intrinsic Force.

In determining the effect of the image attraction on the rate of escape of ions, an ideal surface was assumed devoid of an intrinsic force. While it may be possible that such a surface exists among metals, it is certainly not true for those that are ordinarily used as catalysts.

¹¹ See, for example, R. C. Tolman: "Statistical Mechanics," Chapter 5 (1927).

An iron or copper surface may be oxidized to the point where no effective intrinsic force appears, likewise an aluminum surface covered with a film of oxide possesses a very small intrinsic field. The aluminum surface showed no ability to catalyze the oxidation of ethyl alcohol at temperatures where gold was an excellent catalyst⁶; under similar conditions the catalytic power of the iron and copper oxides was very small.

Poisoning of catalysts on the basis of the proposed hypothesis may largely be due to the formation of a compound on the surface of the catalyst of such a nature that the intrinsic field of the metal becomes neutralized, thus decreasing its ability to dissociate the gas molecules on the surface.

The mathematical treatment for the effect of the intrinsic field is the same as for the image field, with the exception that while the image force is an attraction for ions of either sign so that (work done against the image field) = $e\phi_1 \equiv w_1 > 0$ always, the intrinsic force is an attraction for ions of one sign and a repulsion for ions of the opposite sign, so that the (work done against intrinsic field) = $e\phi_2 \equiv w_2 \geq 0$, depending on the nature of the surface. The field (image or intrinsic) will be called positive when it urges a positive charge towards the surface.

Taking account of the image and intrinsic fields, the concentration of the ions in the chemically active region is

$$n \left(\frac{kT}{2\pi m} \right)^{\frac{1}{2}} e^{-e(\phi_1 + \phi_2)/kT}$$

The Effect of Pressure.

The equation as it now stands, although giving an expression for the rate of reaction, is not sufficiently comprehensive in that it considers only the surface in detail, while the n term alone refers to the reactants.

It will be recalled that n is the ionic concentration in unit volume of gas at the surface. This concentration is obviously determined by two factors, the pressure of the gas, and the nature of the gas, i.e., its dissociation potential.

The effect of gage pressure p on the ionic concentration as given from thermionic studies is

$$n = B e^{-F_1 - w_3/kT}$$

where B is a constant, F_1 and w_3 are functions of p only, and not of T . This can be written.

$$n = n_0 e^{-w_3/kT}$$

where w^3 is the difference in the energy content between an ion on the surface at pressure p and an ion on the surface when the pressure is such that the ionic concentration is n_0 .

The Effect of the Nature of the Gas.

In a previous article⁶ in determining the distance from the surface to which the intrinsic force was effective, the assumption was made that the value of b found from the slope of the curve represented only the work

necessary to get an ion away from the surface, and did not include the energy necessary to complete the dissociation of gas into ions.

This assumption doubtless serves as a fair approximation where it was intended to be applied, namely to the dissociation of ethyl alcohol. Such an assumption, however, cannot be given a general application; for highly polar molecules like ethyl alcohol the electrical forces at the surface are sufficient to so separate the ions that but little external work would be needed to remove an ion from its mate. For non-polar molecules, on the other hand, it would seem evident that the energy necessary to complete the dissociation of the molecule into ions would become very appreciable.

The work w_4 necessary to complete the dissociation of a molecule is expended in removing one ion against the electrical attraction of the other; $w_4 > 0$ always, by an amount determined by the nature of the gas. The previous expression for n must be modified, therefore, by the factor $e^{-w_4/kT}$, which is an obvious application of the Maxwell-Boltzman distribution law.

General Expressions for the Rate of Reaction

The energy of an ion in the chemically active region is thus made up of four parts:

- (1) The work done against the image attraction, $e\phi_1 = w_1$.
- (2) The work done against the intrinsic field, $e\phi_2 = w_2$.
- (3) The energy dependent on the gage pressure, w_3 .
- (4) The energy to complete the dissociation, w_4 .

It will be noted that the first two are determined by the surface and the last two by the gas.

The complete expression for the rate R at which a given kind of ion gets into the chemically active region is, therefore:

$$R = n_0 \left(\frac{kT}{2\pi m} \right)^{1/2} e^{-\frac{w_1 + w_2 + w_3 + w_4}{kT}} \equiv AT^{1/2} e^{-b/T} \quad (6)$$

by putting $bk = w_1 + w_2 + w_3 + w_4$. b is a measure of the work which an ion must do in escaping from the surface to a region where it can react chemically.

The above expression for the rate of escape of ions from a catalytic surface may now be applied directly to the rate of chemical action. Let us consider a condition in which c ions of C , d ions of D , . . . leave the catalyst per sq. cm. of surface per second and enter the chemically active region to form intermediate ionic combination products, S , T , . . . according to the equation



where (*) refers to ions. An ion entering the chemically active region may be either of two types, a simple ion resulting from the initial molecular dissociation, or a complex ion formed by the attachment of the simple ion to a neutral molecule.

In general each kind of ion will have a different rate R of getting into the chemically active region. The forward reaction will be, therefore:

$$R_f = a'_1 A'_C A'_D A'_E \dots T^{(c+d+e+\dots)} e^{-(e_b c + d b_d + e b_e + \dots)/T}$$

$$\equiv a'_1 A' T^{n'/2} e^{-b'/T}$$

$n' = c + d + e + \dots$, is the number of ions contributing to the forward reaction; a'_1 is the fraction of the ions of C, D, E, ... arriving per second in the chemically active region which actually combine to form the intermediate product S, T,

The ionic combination product S, T, ... may be converted into the final reaction product in several different ways: (1), S, T, ... may themselves be the end product; (2) S, T, ... may combine with gases C, D, E, ... in a homogeneous reaction according to the equation



where X, Y, Z, ... are the end reaction products which escape from the image region; or (3), S, T, ... may be drawn back to the surface and again decomposed into C, D, E, (3) will always be in process.

The rate of the forward reaction may now be expressed by

$$dC'/dt = a'_f a'_1 A' T^{n'/2} e^{b'/T}$$

$$\equiv A'_0 T^{n'/2} e^{-b'/T}$$

where a'_f is the proportionality factor referring to the probability of S, T, ... being converted into X, Y,

By setting $E/k = b$, the above expression for the rate of chemical action becomes similar in form to the Arrhenius equation, where E of the latter refers to the "energy of activation". The present development, however, gives the terms an entirely new significance. b , a measure of the work done by the ions in escaping far enough from the surface to react chemically, may best be termed the *chemical work function*. A'_0 containing the terms $a'_f a'_1$ referring to the probability that the ions entering the chemically active region will combine to form the initial and final reaction product may be termed the *combination factor*. Since, as has been stated, an ion does not have to escape from the image region to react chemically, the Chemical Work Function is less than the Thermionic Work Function.

It is to be assumed that chemical combination is divided according to the laws of probability between all processes which bring the required ions and molecules together in the chemically active region. The process most favored by chance under one set of conditions need not necessarily be so under all.

The back reaction is represented by an equation identical to that developed for the forward reaction, but with different values for the constants).

$$dC''/dt = a''_f a''_1 A'' T^{n''/2} e^{-q/T}$$

$$\equiv A''_0 T^{n''/2} e^{-q/T}$$

where q is the heat of formation of s molecules of S , t molecules of T ,

Equilibrium is reached when

$$dC'/dt = dC''/dt$$

and is expressed by the equation

$$K = \frac{(\mathfrak{a}_f \mathfrak{a}_i)_o}{(\mathfrak{a}_f \mathfrak{a}_i)_o} = \frac{A'}{A''} T^{\frac{n''-n'}{2}} e^{-(q-b)/T}$$

where K is the equilibrium constant and $\frac{(\mathfrak{a}_f \mathfrak{a}_i)_o}{(\mathfrak{a}_f \mathfrak{a}_i)_o}$ represents the probability at equilibrium that the average molecule, situated in the chemically active region, will escape from the image zone rather than be drawn to the surface and dissociated.

Deductions

The effect of gases, and the previous treatment of the catalyst on the intrinsic force can only be expressed in a qualitative manner at this time. It is hoped that the continued study of contact difference of potential will add to our knowledge of the factors underlying the intrinsic force. This is important since it follows on the basis of the proposed mechanism that the change in w_2 due to variations in the intrinsic force from point to point over the surface gives rise to the "chemically active center" phenomena established by H. S. Taylor. It has already been suggested that the poisoning of catalysts may be due to the formation of a compound on the surface which materially changes the intrinsic force.

From the argument as presented, it will be seen that if the intrinsic field is uniform over the surface, the Chemical Work Function will be practically independent of the strength of the intrinsic force. Let a case be considered in which the intrinsic field is positive as on gold, then the negative ions will be drawn more closely to the surface while the positive ions will be pushed out. Thus, since the distance r is less for the negative ion than for the positive, the image force will be greater on the negative than on the positive ion, so that $(w_1 + w_2)^+ < (w_1 + w_2)^-$. Since w_4 must be the same for either ion it follows that $b^+ < b^-$ in proportion to the strength of the positive intrinsic field. However, for chemical action to take place both positive and negative ions must enter the chemically active region; hence a concomitant lowering of b^+ and a raising of b^- will have but little effect on the catalytic activity of a surface.

For most substances, on the other hand, it is to be expected that the intrinsic force will vary over the surface, or it might actually change in sign from point to point on a surface like partially reduced iron oxide or a heavy metal impregnated with alkali. In this case the positive ions will enter the chemically active region in greater numbers and with less work from the areas of strong positive intrinsic force, while the negative ions will come more readily from the weak positive or negative areas; therefore, $(b^+ + b^-)$ will

be lower than on a surface of uniform intrinsic force. From this it will be seen that the more irregular the intrinsic force over the surface, the lower will be the Chemical Work Function, and the greater will be the number of molecules reacting per sq. cm. per second, hence the greater the catalytic power.

The writer is especially indebted to Dr. W. E. Deming of this Laboratory for his constructive criticisms and his many valuable additions to the present paper.

Summary

Certain observed facts, namely, the emission of ions during various surface catalyzed chemical reactions following an equation of the Richardson type, and the concentration of these ions increasing as the inverse cube of the distance upon approaching the surface, have been made the basis for the proposed mechanism of surface catalysis, wherein the subject is treated as a special case of thermionic emission in gases.

In brief, the mechanism is that the gas molecules upon approaching the surface are dissociated into ions by the combined image and intrinsic forces of the catalyst. The ions so formed are driven from the surface by kinetic agitation with a probability distribution of velocities. Chemical action results from a combination of the ions whose velocity components perpendicular to the surface are sufficient to carry them out to a region of weak surface forces—the chemically active region.

The equation for rate of the forward reaction developed from the point of view of electrostatics is

$$dC'/dt = A''T^{n'/2} e^{-b'/T}$$

where A is the *combination factor* and b is the complete *chemical work function*.

The back reaction is expressed by the same equation as is the forward but with different values for the constants. Equilibrium, therefore, is expressed by

$$K = \frac{A'}{A''} T^{\frac{n''-n'}{2}} e^{-(a-b)/T}$$

THE ELECTROCHEMICAL BEHAVIOUR OF SILICATE GLASSES. V*
The Electrical Properties of the Anode Layers**

BY J. B. FERGUSON, M. J. MULLIGAN AND J. W. REBBECK

When an electrical current is passed through a sample of glass, the electrical properties of the sample will be changed if the glass composition is thereby altered. The nature and extent of some of these changes are discussed in this paper.

Experimental Methods

The samples were prepared in the form of test-tubes, 6-8 cm. long, 11 mm. bore and 0.7 mm. wall thickness. The upper ends of these were sealed to smaller tubes of the same glass which were 30 cm. long, 4 mm. bore and of the same wall-thickness. One electrode material was placed inside a sample tube which was held in a thick-walled Pyrex test-tube containing the other electrode material. In order to prepare an anode layer using mercury as anode, the sample tube was filled with mercury by distillation at low pressures to a point several centimeters above the seal. After the electrolysis, the mercury was pipetted out until the level was just below the seal and measurements were carried out with the electrode in this condition. Other electrode materials were simply poured into the tubes. Aqueous solutions were covered with paraffin. When powdered graphite was employed, it was pressed into place and to facilitate this sample tubes of a uniform wide bore were used. At temperatures up to and including 100°C the outer electrode material was usually an aqueous solution of sodium hydroxide, 5 wt.%, and above this temperature mercury was employed. When other materials were used, they are indicated in the text.¹

Current measurements were made by determining the drop in potential across a standard resistance by means of a precision potentiometer, the readings being proportional to the current flowing in the circuit. Nichrome, silver and platinum wires were used to make connections with the electrode materials. These wires were insulated with rubber or glass where this was possible as an additional precaution against electrical leakage. The latter was observed by withdrawing the inner electrode wire to a point just above the electrode surface and taking a reading. The leakage was kept down to a negligible quantity by shielding and insulating the electrical circuits. Parasitic currents in the potentiometer circuit were detected by means of an elimination switch as suggested by White.²

* Contribution from the Department of Chemistry, University of Toronto.

** This investigation was carried out with the assistance of The National Research Council of Canada. Mr. Mulligan held successively three scholarship awards from them: a Bursary, a Studentship and a Fellowship.

¹ A more detailed account of the experimental procedure may be found in earlier papers of this series: Rebeck and Ferguson: *J. Am. Chem. Soc.*, 46, 1991 (1924); Rebeck, Mulligan and Ferguson: *J. Am. Ceram. Soc.*, 8, 330 (1925). References for glass analyses may be found in Part III, Mulligan, Ferguson and Rebeck: *J. Phys. Chem.*, 32, 779 (1928).

² W. P. White: *J. Am. Chem. Soc.*, 36, 1868 (1914).

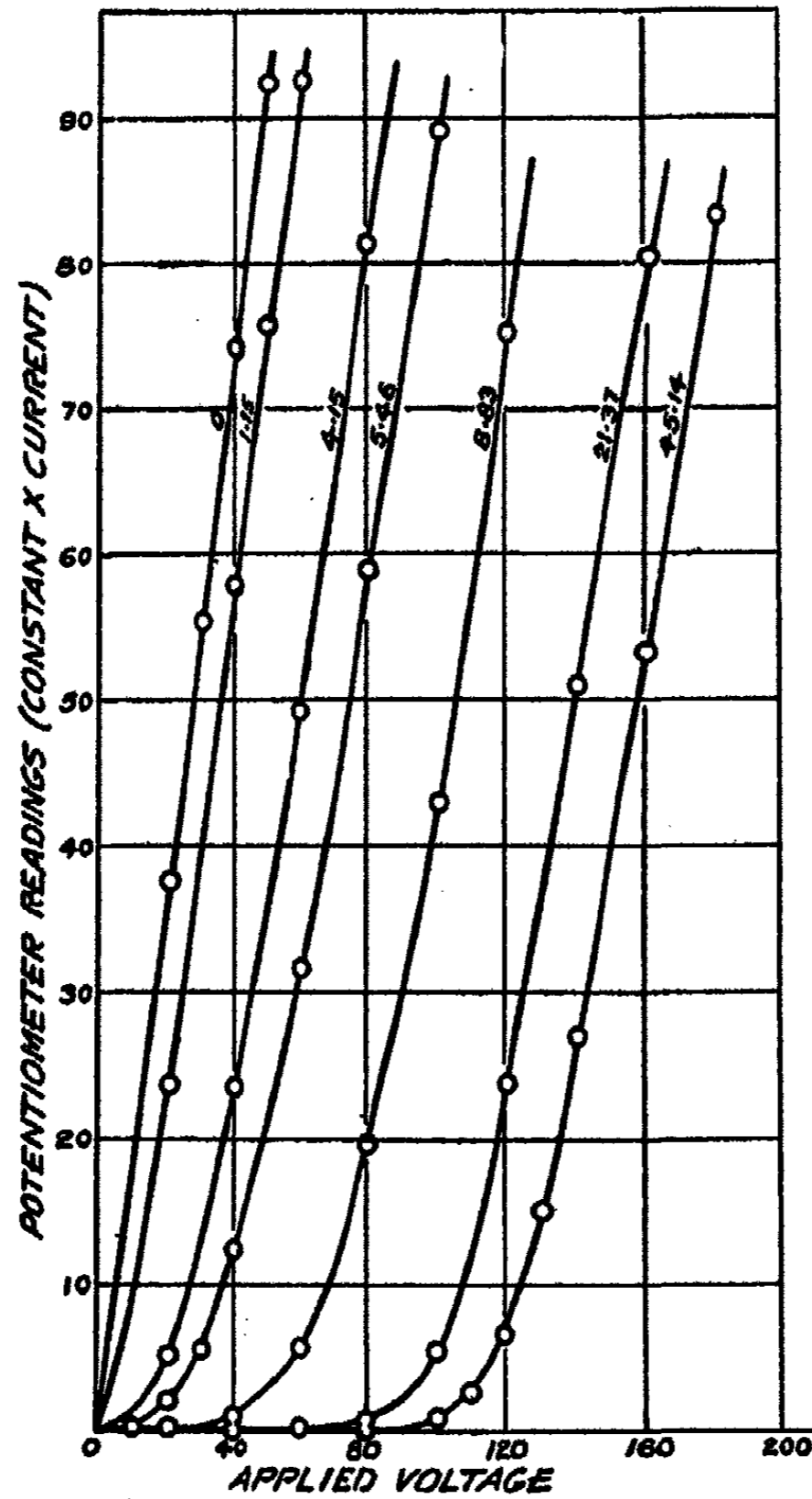


FIG. 1

The current-voltage relation for tube 606 D after different periods of electrolysis with a mercury anode.

The Effect of Electrolysis on Current Reading

Since the passage of current through glass is almost entirely due to the cations, the magnitude of this current is naturally very dependent upon the kind of anode in use. If the anode material is readily soluble the current does not change very much during an electrolysis at constant applied voltage but if the anode material is difficultly soluble the current decreases rapidly as the electrolysis proceeds. Corresponding voltage changes occur when the electrolysis is carried out at constant current instead of at constant applied voltage. The current decrease is brought about by the formation of a film of glass

at the anode, the so-called anode layer, in which the conduction process does not appear to be identical with that of the original glass. For example, the current does not increase with the applied voltage in accordance with Ohm's Law. The electrical properties of these anode layers have been noted by many investigators but none appear to have studied the dependence of the current-voltage relation upon the time of electrolysis with the difficultly soluble anode.

Mercury is a good example of a difficultly soluble anode material.¹ The dependence of the current-voltage relation on the time of electrolysis was studied with sample tube No. 606 D of new soda-lime glass using a mercury anode in the following manner.²

The electrolysis was carried out at 100°C using 110 volts. The measurements were made from time to time at various voltages which were progressively increased for these during any one series. The amount of electrolysis which took place during the measurements could safely be neglected in computing the total time of electrolysis at this temperature. A graph of the results is given in Fig. 1.

The zero curve indicates for the original glass an Ohm's Law relation. A straight line through the points would not exactly pass through zero voltage on the plot. The deviation is slight and is due to certain E.M.F.'s of a chemical nature which were set up in the system. These will be discussed later. The lower portions of the other curves represent the nearly constant values to which the readings fell after applying the voltage. As this was increased the differences between the initial and final readings became less and on the nearly straight portions of the curves at high voltages these differences were negligible. This fact made possible the rapid measurement of the current at the higher voltages and thus reduced the possible error from electrolysis during measurement. The actual readings upon which the graph is based are given in Table I.

The measurements must not be regarded as exact determinations although the experiments were carefully conducted. The initial high current reading observed in many cases, first rapidly and then slowly decreased so that the final reading taken was to some extent a matter of individual judgment. When the applied voltage was just below that required to give readings at the lower end of the straight portion of the curve for the electrolysed tube, in some cases the initial current fell slightly and then rose. The double entries in the last column in the table represent the minimum values and the final nearly constant values. In spite of such uncertainties, the results indicate the general character of the current-voltage relation.

A great many experiments were made, the details of which need not be given here. Similar types of curves were obtained at 100°C with the following glass samples:

¹ This point has been discussed in Part IV, Mulligan, Ferguson and Rebbeck: *J. Phys. Chem.*, 32, 843 (1928).

² New glass signifies glass which has not received any especial thermal, electrical or other treatment.

TABLE I
Current-voltage measurements with tube 606D
Potentiometer reading in millivolts after hours of total electrolysis indicated at head of each column

| Applied Voltage (volts) | 0 | 1.15 | 4.15 | 5.46 | 8.83 | 21.37 | 45.14 |
|-------------------------|------|-------|------|------|------|-------|-----------|
| 0 | | | | | | | |
| 10 | | | | 0.25 | | | |
| 20 | 37.6 | 23.7 | 5.2 | 2.0 | 0.2 | | |
| 30 | 55.6 | | | 5.7 | | | |
| 40 | 74.2 | 58.0 | 23.6 | 12.5 | 1.0 | 0.03 | 0.03 |
| 50 | 92.5 | 75.85 | | | | | |
| 60 | | 92.7 | 49.4 | 31.7 | 5.75 | 0.1 | 0.08 |
| 80 | | | 81.4 | 59.0 | 19.7 | 0.7 | 0.15 |
| 100 | | | | 89.2 | 43.1 | 5.5 | 1.0 |
| 110 | | | | | | | 2.6 |
| 120 | | | | | 75.2 | 23.9 | 6.5-8.0 |
| 130 | | | | | | | 15.0-16.3 |
| 140 | | | | | | 51.0 | 27.0 |
| 160 | | | | | | 80.2 | 53.4 |
| 180 | | | | | | | 83.2 |

(a) New soda-lime glass with mercury-containing anode layers formed at various temperatures ranging from 100 to 275°C using 110 volts, and at 100°C with voltages ranging from 30 to 220 volts.

(b) Annealed soda-lime glass with mercury-containing anode layers formed at 100 and at 185°C with 110 volts.

(c) New and annealed soda-lime glass with anode layers formed at 100°C using a carbon anode and 100 and 220 volts.

(d) New soda-lime glass with an anode layer formed at 450°C using a carbon anode and a tin cathode.

(e) New glass, Schott type 59^{III}, with mercury-containing anode layers formed at 100 and at 275°C using 110 volts.

The form of the curves suggests that the lowered current reading on electrolysis is due to an increase in the true ohmic resistance and to a counter E.M.F. which is set up. An experimental study of these factors was accordingly carried out.

The tentative theory would indicate that the true resistance of the electrolysed glass sample could be approximately determined from the slope of the upper nearly straight portion of the current-voltage curve. From this determination the resistance of the mercury glass film could be calculated. If the hypothesis were correct, and the mercury glass film were similar to other known glasses, the change of this resistance with temperature would follow the rule of Rasch and Hinrichsen:¹ $\log \rho = A/T + B$ A tube of new

¹ Rasch and Hinrichsen: *Z. Elektrochem.*, 14, 41 (1908); Baumeister: *Diss. Rostock* (1912); Ambronn: *Ann. Physik*, 58, 139 (1919); Holladay: *J. Franklin Inst.*, 195, 229 (1923); Schönborn: *Z. Physik*, 22, 305 (1924); Rebbeck, Mulligan and Ferguson: *J. Am. Ceramic Soc.*, 8, 329, 545 (1925); Ferguson: *Can. Chem. Met.*, 10, 131 (1926); Schiller: *Arch. Elektrotech.*, 17, 609 (1927); *Ann. Physik*, 83, 137 (1927).

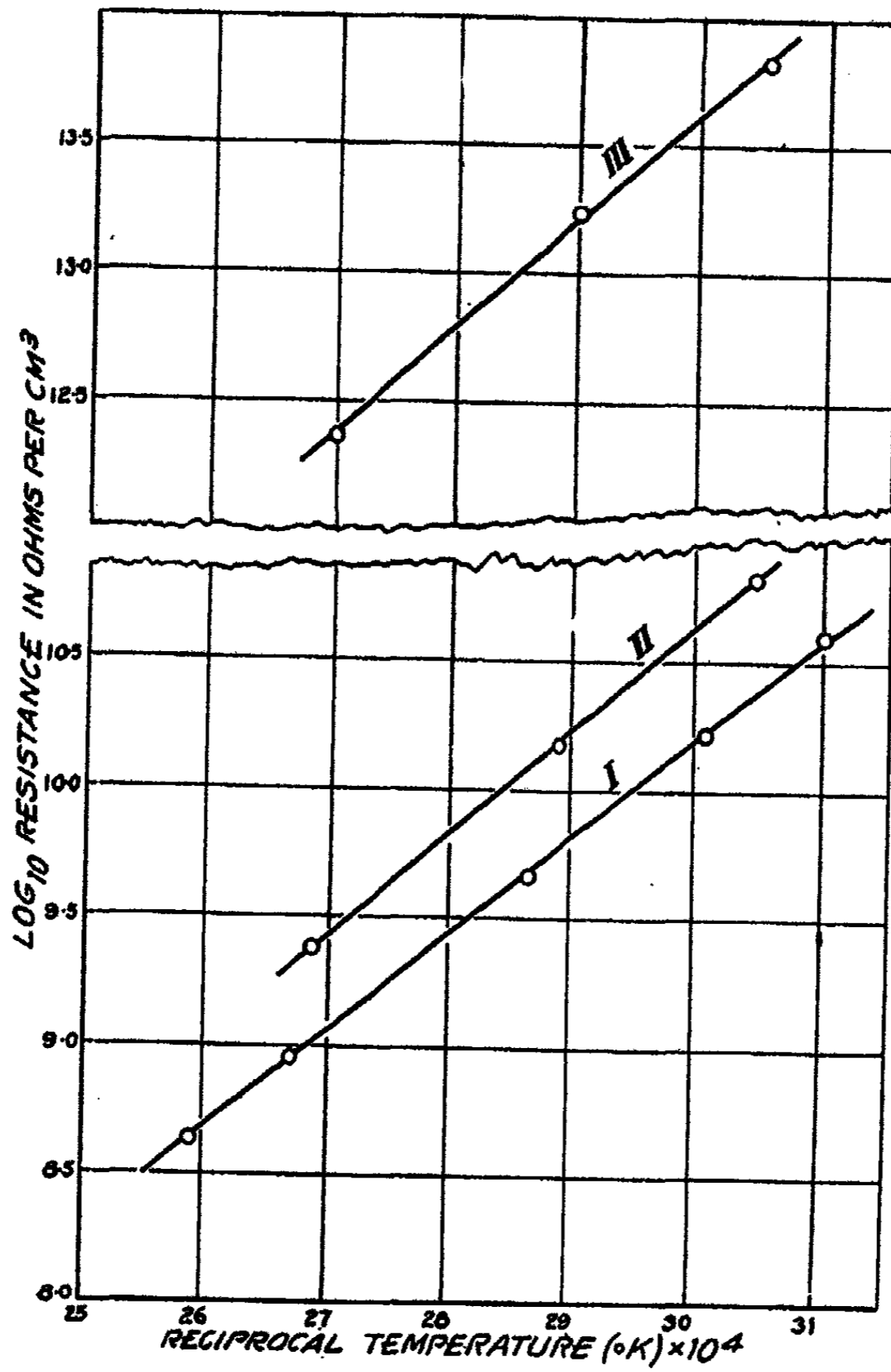


FIG. 2

Curve I. The resistance of the original glass sample.
Curve II. The resistance of the electrolysed glass sample.
Curve III. The true resistance of the mercury-containing anode glass layer.

soda-lime glass was therefore electrolysed for 35 minutes at 270°C with 110 volts using mercury for both cathode and anode liquids. The cathode mercury was then replaced by an aqueous solution of sodium hydroxide of the usual strength and current-voltage measurements were carried out at 55.5, 73.2 and 99.2°C. In order to get measurements on the straight portions of the curves, it was necessary to use from 296 to 390 volts.¹ The results of these experiments are given graphically in Fig. 2. The resistance of the original glass is indicated by curve I, the resistance of the electrolysed glass sample by curve II and the resistance of the mercury glass film by curve III. The last mentioned resistance was calculated on the further assumptions that the film was 0.5 μ thick and continuous. Other experiments were carried out with other samples at temperatures ranging from 65.2 to 139°C. These confirmed the results just given and also indicated that the rule would probably hold at 139°C if the errors due to electrolysis during the measurements could be eliminated.

The counter E.M.F.'s set up during an electrolysis with a difficultly soluble anode may be calculated from the current-voltage curve or may be directly observed. The direct determination of these was carried out in two ways. In one, the source of the applied potential was disconnected from the circuit which was then closed and the potential difference initially set up across the standard resistance in series with the sample tube was determined by means of the potentiometer. From this reading the counter E.M.F. was calculated. In the other method, the applied voltage was quickly reduced and the voltage which would just prevent a current flowing in the opposite direction was determined. The galvanometer of the potentiometer circuit was used to indicate the balance. When the counter E.M.F. was above 100 volts, both methods gave low results but the second method was the better. The experiments could not be carried out with sufficient rapidity by these methods. In all such cases of suspected low results slight changes in technique which increased the speed with which the measurements could be made gave rise to higher results. A number of our results which were obtained at 100°C with soda-lime glass samples having mercury-containing anode glass layers are given in Table II. The calculated values agree so well with the observed values that the hypothesis appears to be well grounded.

After a glass sample has been electrolysed for a long time with a mercury anode, the apparent resistance does not change much with change of temperature. This has been noted by others in their experiments at higher temperatures.² In our experiments the mercury glass has been found to show a normal temperature coefficient of resistance and the former effect has been therefore attributed to the counter E.M.F.'s which are set up. This was checked in the following manner. Current-voltage curves were obtained at various temperatures. The nearly constant counter E.M.F. which is obtained at the

¹ We wish to thank the Department of Physics for certain apparatus used in these experiments.

² Warburg: *Wied. Ann.*, 21, 622 (1884); LeBlanc and Kerschbaum: *Z. physik. Chem.*, 72, 468 (1910); Schulze: *Ann. Physik*, 37, 435 (1912).

TABLE II
Examples of counter E.M.F.'s at 100°C

| Tube No. | Applied Voltage | Counter E.M.F. | | Exp. Series |
|----------|-----------------|----------------|------------|-------------|
| | | Observed | Calculated | |
| 608D | 20 volts | 19.5 volts | 19.8 volts | A |
| | 40 | 39.5 | 39.6 | |
| | 60 | 59.5 | 59.2 | |
| | 80 | 76 | 78 | |
| 606D | 60 | 59 | 59.8 | |
| | 80 | 79 | 79.5 | |
| | 100 | 96.6 | 98.9 | |
| | 110 | 104 | 107.7 | |
| 592A | 100 | ca. 85 | | |
| | 150 | ca. 85 | | |
| 610D | 80 | 65 | 65 | |
| | 120 | 66 | 65 | |
| 625D | 140 | 86 | 86 | |
| 611D | 220 | 168 | 187 | |

TABLE III
Examples of counter E.M.F.'s calculated from current-voltage curves obtained at different temperatures

| Tube No. | Applied Voltage | Counter E.M.F. | Temperature °C | Series |
|----------|-----------------|----------------|----------------|--------|
| 615D | 320-290 volts | 203.6 volts | 73.2 | A |
| | | 200.5 | 138.8 | |
| | | 231 | 73.2 | B |
| | | 231 | 55.5 | |
| 608D | 120-160 | 99.8 | 100 | B |
| | 120-200 | 99.8 | 123.5 | |

higher voltages was determined graphically from each curve. The values found are given in Table III and support the suggestion just previously made.

Earlier in this paper we have briefly summarized the conditions under which we have obtained current-voltage curves similar to those given in Fig. 1. The fact that such curves were obtained in these cases seems sufficient to warrant the assumption that the conduction processes were not essentially different from that which we have more fully investigated.

When the glass tubes were electrolysed with mercury as cathode and a dilute solution of sodium hydroxide as anode, the current readings decreased

slightly as the electrolysis proceeded. This decrease appeared to be mainly due to the counter E.M.F.'s set up. When a tube which had been so electrolysed for a long time was short-circuited, the current fell rapidly at first and then continued for a long time at a practically constant value. The counter E.M.F.'s were therefore of two kinds, one of which rapidly decreased and one which persisted for a long time. The first type were similar to those observed with the mercury anode but these were only a few volts. However when the sodium hydroxide solution was replaced with a solution of mercuric chloride, the current fell more rapidly as the electrolysis proceeded and the value of the counter E.M.F. of this type more nearly approached that found when the anode was metallic mercury. The second type were from 1 to 3 volts and are the result of a chemical polarization. When a tube was set up for electrolysis, with a mercury cathode and a sodium hydroxide solution anode, the various contact potentials in the electrical system gave rise to a measurable current which corresponded to that obtained with an applied voltage of 0.2 to 0.5 volts depending on the particular arrangement and on the tube. Slightly higher values were observed when the tube was washed out with the dilute sodium hydroxide solution and dried by evacuation before filling with mercury. An actual increase of 2.83 volts was noted with tube No. 481D

TABLE IV

Examples of the counter E.M.F.'s of a chemical nature which are obtained after a preliminary electrolysis using 110 volts, sodium hydroxide solution as anode liquid and mercury as cathode liquid.

| Tube No. | Time electrolysed | Counter E.M.F. | Temperature |
|----------|-------------------|-----------------------------|-------------|
| 469D | 0 minutes | 0.35 volts | 100°C |
| | 1 | 0.81 | |
| | 2 | 1.13 | |
| | 4 | 1.37 | |
| | 18 | 1.97 | |
| | 40 | 2.13 | |
| | 107 | 2.20 | |
| | 263 | 2.24 | |
| 58A | 21.1 hours | 1.9 after 35 sec. discharge | 75°C |
| | | 1.7 " 405 " " | |
| 60D | 20.2 " | 1.9 " 32 " " | 75°C |
| | | 1.7 " 420 " " | |
| | 191 " | 2.7 " 15 " " | 75°C |
| | | 2.1 " 70 " " | |
| | | 1.9 " 130 " " | |
| 54A | 22.6 " | 1.9 " 30 " " | 75°C |
| | | 1.8 " 1020 " " | |

when 0.25 cc. of a concentrated sodium amalgam was added to the cathode mercury. This decreased to 2.45 volts after an electrolysis of several hours but did not further change in an additional electrolysis of 0.5 hours. Counter E.M.F.'s of this type could easily result from the liberation of sodium at the cathode during the electrolysis of the sample. Typical examples of these are given in Table IV.

The idea that the lowered current reading obtained after a prolonged electrolysis of a glass sample was mainly the result of a type of polarization was first advanced by Buff.¹ The explanation has been used by many others since that time,² but the phenomenon has not previously been systematically investigated. In the electrolysis of crystals, large counter E.M.F.'s are also encountered³ and similar effects have been noted with such materials as porcelain.⁴ Sinjelnikoff and Walther⁵ believe that they are the important factors in the electrical behaviour of dielectrics.

Investigators who have studied the conduction of glass at a temperature of several hundred degrees⁶ have not found it necessary to use this explanation in order to interpret their results. Schulze was able to correlate his observations on the assumption that a glass sample with a mercury-containing glass anode layer behaved as a capacity in series with a high resistance. The anode layer was the dielectric and the original glass the high resistance. In applying this explanation to our results difficulties are encountered. When the counter E.M.F. is very near the applied voltage, the discharge curve for a tube resembles very closely the discharge of a telephone condenser connected in series with a similar tube of original glass. This experimentally determined fact tends to support the idea but our observations, that at the higher applied voltages the counter E.M.F. is nearly independent of the applied voltage, cannot be reconciled with it. In order to account for such a peculiar charging of the glass condenser, one would have to assume that the conduction in the anode layer was dependent upon the applied voltage in an equally peculiar fashion.

Whether the conduction processes at high and low temperatures differ in kind or merely in the importance of the factors involved can hardly be determined from the experimental work available. The true resistance of mercury anode glass has been found by us to vary with the temperature in accordance with the rule of Rasch and Hinrichsen and it is reasonable to assume that this would be the case at the higher temperatures. The small temperature coefficient reported by Schulze is at variance with this assumption if his resistance values represent the true resistance of this kind of glass.

¹ Buff: *Ann. Chem. Pharm.*, 90, 257 (1854).

² Beetz: *Pogg. Ann.*, 92, 452 (1854); T. Gray: *Phil. Mag.*, (5), 10, 226 (1880); A. Gray and Dobbie: *Proc. Roy. Soc.*, 63, 38 (1898); 67, 197 (1900); Schröder: *Z. physik. Chem.*, 26, 367 (1913); Schiller: *Ann. Physik*, 74, 105 (1924); Mundel: *Arch. Elektrotech.*, 15, 320 (1925).

³ Joffe: *Ann. Physik*, 72, 461 (1923); Schiller: 83, 137 (1927).

⁴ Brace: *Trans. Am. Electrochem. Soc.*, 33, 205 (1918).

⁵ Sinjelnikoff and Walther: *Z. Physik*, 40, 786 (1927).

⁶ LeBlanc and Kerschbaum: *loc. cit.*; Schulze: *loc. cit.*

If we consider the acting voltage as the difference between the counter E.M.F. and the applied voltage, the conduction in our mercury-containing glass layers follows Ohm's Law. These layers were very thin and the potential drop across the layer on the sample used in the experiment described in connection with Fig. 2 must have represented a high average potential gradient. The conduction of electricity by glass when such potential gradients are used has been studied by many investigators. Quittner¹ has recently found that Faraday's Law is obeyed. The current-voltage relation discovered by Poole² has been found by Schiller to hold under a variety of experimental conditions. This relation may be written: $\log i = C + DX + \log X$ in which i is the current, C and D are constants and X is the average potential gradient. A somewhat similar equation fits approximately the lower part of our current-voltage curves for glass with mercury-containing glass anode layers. The equation is $\log i = A + BE$ in which A and B are constants and E is the applied voltage. It fits fairly well the values given by Warburg³ for his glass with a mercury-containing anode layer although his experiments were conducted at high temperatures. Warburg was not aware that mercury could enter glass but has since agreed with the findings of Schulze.⁴

It does not fit the results of LeBlanc and Kerschbaum⁵ which are best represented by the equation $i = KE^2$. This relation is also the one proposed by Mundel⁶ as the result of his studies of glass conduction at high voltages. The significance of these agreements is not apparent but it seemed wise to point them out at this time.

The great influence which electrode conditions may have on the resistance values observed with materials like glass is a matter of common knowledge. If the counter E.M.F.'s which nearly equal the applied voltages are involved, slight changes in the electrode conditions might easily cause large changes in the acting voltage and give rise to the effects noted.

Experiments on Current Reversal

The chemical effects associated with current reversal on tubes containing mercury and certain other anode glass layers have been dealt with in detail in the previous paper. The electrical effects will now be discussed.

Tube No. 317D was electrolysed with 80.5 volts at 76°C for 16.2 hours using a mercury anode. Measurements were then carried out at 74.45°C using 85 volts. Readings were taken as in the ordinary current measurements. An initial reading was taken with the original glass and another reading at the end of the preliminary electrolysis. The mercury was made cathode and a series of readings were taken. The mercury was made anode and the readings

¹ Quittner: Sitz. Akad. Wiss. Wien, 136, IIa, 151 (1927).

² Poole: Phil. Mag., 42, 488 (1921); Schiller: Z. tech. Physik, 11, 588 (1925); Ann. Physik., 81, 32 (1926); 83, 137 (1927); Arch. Elektrotech., 17, 609 (1927).

³ Warburg: loc. cit.

⁴ See Ann. Physik, 37, 441 (1912).

⁵ LeBlanc and Kerschbaum: loc. cit.

⁶ Mundel: Arch. Elektrotech., 15, 320 (1925).

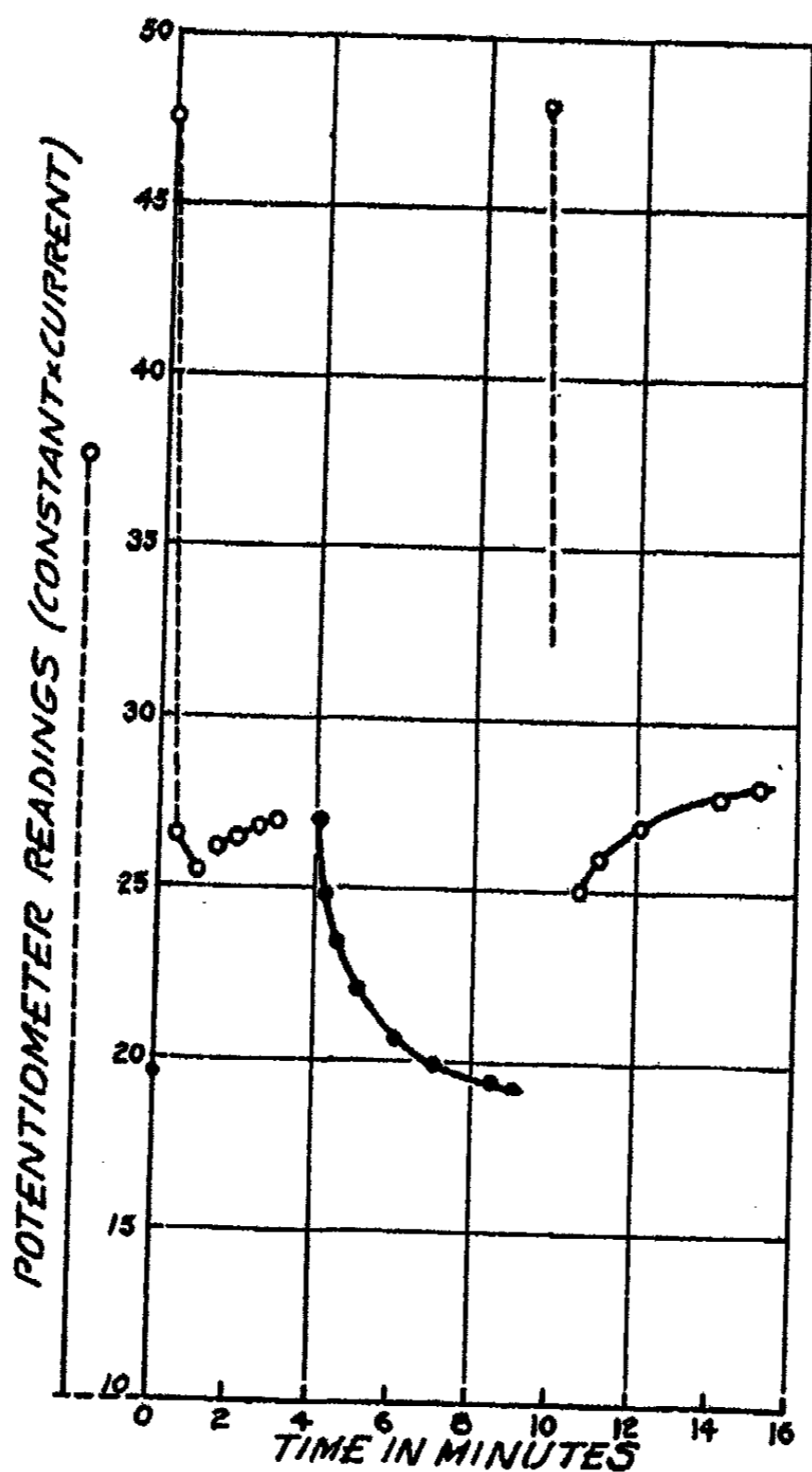


FIG. 3

The effect on the current readings produced by the reversal of the direction of the current, (tube 317 D).

continued. The experiment was again repeated in so far as it related to the last two series of measurements. The results are indicated by Fig. 3. The points on the vertical line to the left are the initial and final readings of the electrolysis proper. The circles on the graph are the readings with mercury cathode, the dots the readings with mercury anode. The high initial reading with mercury cathode would appear to indicate that the acting voltage was the applied plus the counter E.M.F. The course of the curve of such readings with mercury cathode is, we believe, mainly the result of a decrease in the counter E.M.F. and a puncturing of the anode layer. The course of the curve obtained with mercury anode would indicate a rapid healing, as it were, of

these punctures. A similar series of measurements was made with tube No. 477D which had been given a preliminary electrolysis at 100°C using 110 volts for 12 hours. The experimental conditions were however slightly different and the results are therefore given in Fig. 4.

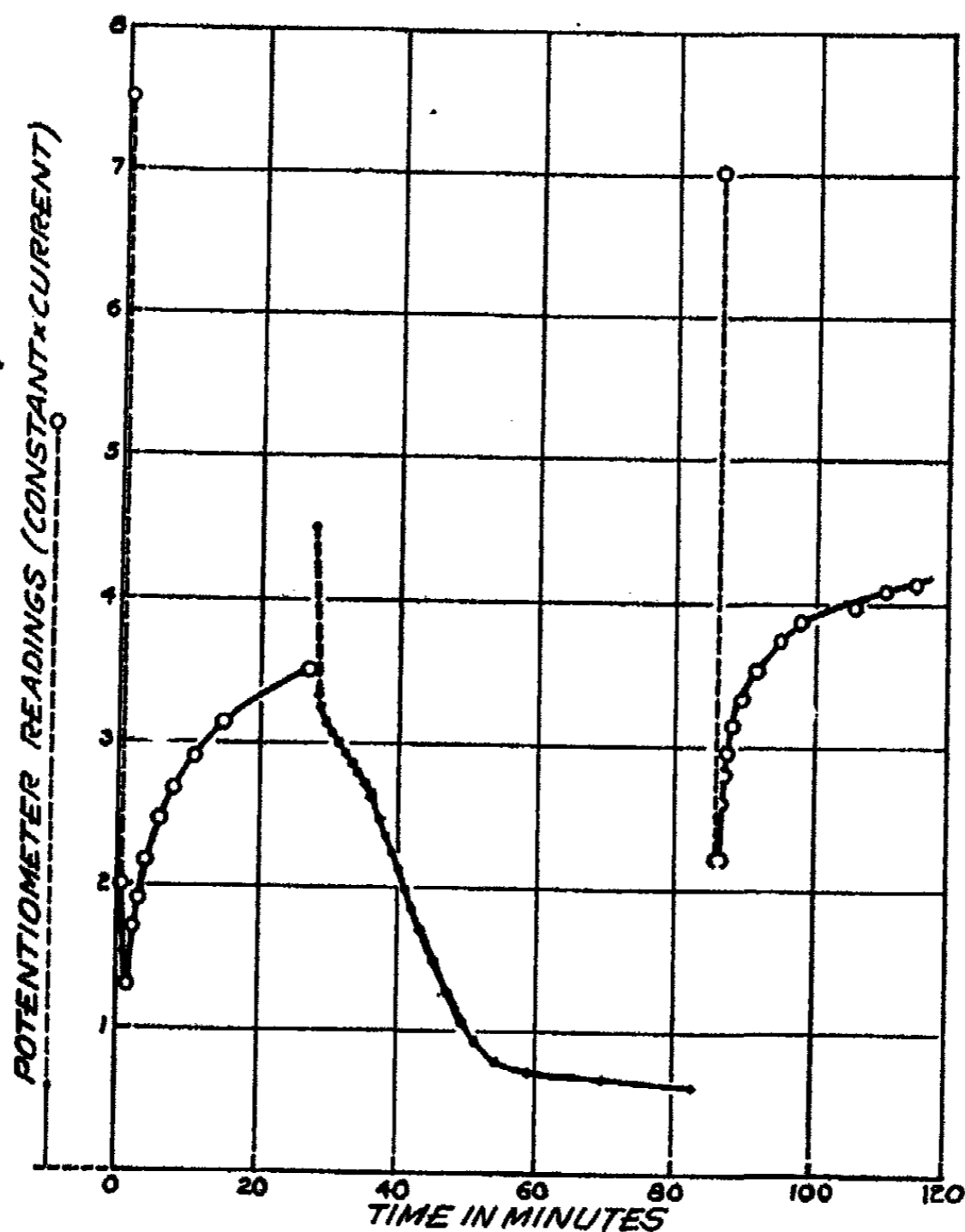


FIG. 4

The effect on the current readings produced by the reversal of the direction of the current, (tube 477 D).

These differ from those indicated in Fig. 3 in that the longer electrolysis with mercury cathode necessitated a longer electrolysis with mercury anode to restore the lowered current reading.

Residual Charge

Hopkinson¹ reported the reversal of the direction of the discharge current during the discharge of a flask which had previously been charged negatively for many hours and positively for five minutes. An attempt was made to

¹ Hopkinson: Phil. Trans. Roy. Soc., 167, 599 (1877).

obtain a similar result under better defined conditions. Tube No. 472D was electrolysed for 18 hours at 100°C with 110 volts using a mercury anode and a dilute sodium hydroxide solution as cathode. The solution was removed from the container and the tube and container well washed. They were dried with the vacuum pump and mercury distilled into the container to the level of the anode mercury. The mercury originally anode was made cathode for 6 hours. The current was then observed after the external source of potential was disconnected. The initial reading was -1000 scale divisions and rapidly increased to +40. After 6 minutes it was +30. The high initial reading was undoubtedly the usual counter E.M.F. reading obtained with a sample having a mercury glass anode layer and the smaller positive reading was probably due to a chemical polarization similar to that obtained when a tube is electrolysed with mercury cathode. Once the tube was prepared, duplicate readings could be obtained by applying the voltage for a short time with the initial anode mercury as cathode.

Summary

1. When a glass sample is electrolysed at moderate temperatures with a difficultly soluble anode material like mercury, the current decreases as the electrolysis proceeds. This decrease is caused by the setting up of counter E.M.F.'s and by an increase in the true resistance of the glass sample. At low voltages the counter E.M.F. may nearly equal the applied voltage but at higher voltages the counter E.M.F. tends to assume a constant value. The minimum voltage which is required to give this nearly constant value increases as the electrolysis proceeds. The true resistance of a mercury-containing anode glass layer has been found to be many times that of the original glass and to change with temperature in accordance with the rule of Rasch and Hinrichsen.
2. The smaller counter E.M.F.'s of constant values which are noted when glass samples are electrolysed with a soluble anode and a mercury cathode are chemical in origin.
3. The manner in which the electrical measurements are affected by current reversal has been indicated for glass samples having mercury-containing anode glass layers.
4. Hopkinson's experiment on residual charge has been repeated under new conditions.

*Toronto, Canada,
October, 1927.*

OPTICAL ISOMERS OF CYSTINE AND THEIR ISOELECTRIC SOLUBILITIES

BY JAMES C. ANDREWS AND EDWIN J. DEBEER*

The comparative physical properties of the possible optical isomers of cystine have never been clearly defined although it has been observed that cystine samples of different optical activities have different isoelectric solubilities in water. It has been suggested that some of the anomalies in the chemical behavior of this substance may also be the result of varying proportions of different optical isomers and furthermore, the peculiar selective action which biological agents frequently show for one optical isomer as opposed to the other makes desirable a more minute acquaintance with these isomers. The present work was undertaken to determine the solubilities in water of isoelectric samples of cystine of different $[\alpha]_D$ values with a greater accuracy than heretofore and to use these figures in their relation to the $[\alpha]_D$ values to deduce what isomers might be present in samples of various activities. It was hoped that the work might ultimately make possible a more exact separation and characterization of the optical isomers of this compound.

The usual formula for the number of optical isomers possible (2^n , where n = the number of asymmetric carbon atoms) points to four compounds in addition to racemic compounds; but here, owing to the symmetry of the whole molecule, two of the isomers are identical and only three configurations of the molecule are possible. To illustrate this more clearly, the two asymmetric carbon atoms may be designated as X and Y, a prefixed plus or minus sign indicating dextro- or laevo-activity.



Combination (1) would indicate laevo, (2) dextro, and (3) and (4), being identical since X and Y are, in this compound, interchangeable, both represent the internally compensated or meso form. There is also the possibility of an optically inactive compound being formed of equimolar parts of dextro and laevo, according to the equation,



this equilibrium being controlled chiefly by the prevailing temperature. Each of these phases is a chemical entity and, as such, has its own physical properties such as solubility, melting point, etc. which, for two enantiomorphous substances are regarded as being identical. If then a solution is saturated with respect to one phase, the introduction of another phase should give increased solubility which would be the sum of the solubility values of the two

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individuals provided the sample be sufficiently large to maintain both solid phases. The possibility that the presence of one phase may affect the solubility of the other seems, in such dilute solutions, to be negligibly slight.

Although solubility figures for cystine are few in number and not in good agreement, they do show definite variations with varying $[\alpha]_D$ values. Inactive samples seem to be more soluble than laevo and Mörner obtained figures which indicate that the dextro variety is also more soluble than the laevo. His figures as well as those of other investigators are given in Table I.

| Specific Rotation $[\alpha]_D$ | Solubility in gm. per l | Temperature ° Centigrade. | |
|--------------------------------|-------------------------|---------------------------|----------------------------------|
| "Laevo" | 0.19 | 20.0 | Hoffman and Gortner ¹ |
| "Laevo" | 0.113 | | Neuberg and Meyer ² |
| -224.3° | 0.111 | 17.0 | Mörner ³ |
| -66.0° | 0.333 | 17.0 | Mörner ³ |
| -5.5° | 0.250 | 17.0 | Mörner ³ |
| "Inactive" | 0.490 | 20.0 | Hoffman and Gortner ¹ |
| "Inactive" | 0.326 | | Neuberg and Meyer ² |
| +47.0° | 0.344 | 17.0 | Mörner ³ |

As far as can be determined, no account was taken, in any of the above determinations, of the possible effect of variations in size of solid sample. It is impossible to say, except in the light of further experiments, how many phases were really in equilibrium with the solution.

Experimental

Cystine samples of different optical activities were purified by making at least five isoelectric precipitations from HCl solution, using dilute NaOH for neutralization. In all cases, a "c.p." cystine, giving a negative Millon test, was used as the starting point. Particular care was always taken in the neutralization not to carry the solution to a pH even as high as 7. The precipitate was then washed repeatedly with distilled water until the washings were electrolyte free, as determined by testing for chloride ion. The purified substance was kept in a desiccator. Nitrogen determinations by the Kjeldahl method gave almost theoretical results and sulfur determinations, when made, have always given results corresponding very closely to the purity obtained by Kjeldahl. After washing the sample electrolyte-free, it was always examined minutely under the microscope for the purpose of detecting any irregularity in crystalline form. The standard method, recommended by Andrews⁴, was followed in determining the specific rotation. Readings were made with a Schmidt and Haensch polariscope, sensitive to $\pm 0.01^\circ$, using a four decimeter tube.

The solubility measurements were made by placing weighed amounts of the samples with definite quantities of twice-distilled water in Pyrex Kjeldahl flasks, which were then tightly stoppered and deeply immersed with frequent

shaking for at least 24 hours (in some cases for weeks) in a Freas water thermostat kept at $25^{\circ}\text{C} \pm 0.05^{\circ}$. The pH of the water used, as checked by the indicator method, was what would result from equilibrium with atmospheric carbon dioxide (about pH 6) and after saturating with the cystine, no detectable change in pH could be observed. The solution was then filtered at 25°C through one or more layers of hardened filter paper and the amount dissolved was determined by making four or five duplicate analyses, using the Folin-Looney colorimetric method. Each analysis was checked against a separate and independently measured standard. In order to place the solubility figures on a more fundamental basis, micro-Kjeldahl determinations were occasionally run against ammonium sulfate standards. The agreement with the Folin-Looney results was excellent and the Folin-Looney method was then used for most of the work because of its greater speed and convenience. As a rule the Folin-Looney procedure gave more consistent results with less trouble. The observed rotation of the solution was also read in a 4 dm. tube at 29°C . These readings could be duplicated to within $\pm 0.01^{\circ}$.

Table II shows a summary of the results obtained. The individual figures for each determination are tabulated, as well as the average figure adopted. It will be noted that all "A" samples consist of 0.05 gm. cystine per 100 cc. water (a figure only slightly above the solubility previously reported for l-cystine), "B" samples consist of ten times the weight of solid in "A," "C," ten times that of "B," and "D," where necessary, twice that of "C." Thus in the samples with greater excess of solid, an opportunity is given for phases present in comparatively small amounts to attain saturation. The necessity for this is amply shown in the table.

Since the determinations were carried out using ordinary distilled water, it was thought well to determine if dissolved CO_2 and the resulting acidity produced any change in the solution figures, although the very flat isoelectric range determined by Merrill⁶ made it seem unlikely. Analyses were therefore made of solutions which had been constantly swept in the thermostat with a slow stream of very pure nitrogen. No appreciable difference in results could be detected. While the actual isoelectric point of cystine is on the acid side of pH 7, the difference between the presence or absence of such amounts of carbon dioxide as could result from contact with ordinary air evidently has no detectable effect.

Theoretical

These data present several interesting features. The presence of at least two phases is indicated in all samples by the fact that large proportions of solid were required to give plateau solubility figures. The 204.2° lot gives a low solubility value of 0.083 gm. per liter in the "A" sample, with a residue consisting of hexagonal plates as shown on microscopical examination, and a plateau figure of 0.163 gm. per liter for the "B" and "C" samples. The observed rotation (*not* the specific rotation) of all the samples was about -0.13° indicating a constant concentration of the laevo phase. The fact that the usual hexagonal crystals made up the residue of the "A" sample confirms

TABLE II

| [α] _D ²⁰ of sample | % N | A | | B | | C | | D | | | |
|------------------------------------------------------|--------|----------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|--------|-------|
| | | 0.05 g. per 300 cc. [α] _D ²⁰ Solubility g. per l. | 0.05 g. per 300 cc. [α] _D ²⁰ Solubility g. per l. | 0.5 g. per 300 cc. [α] _D ²⁰ Solubility g. per l. | 0.5 g. per 300 cc. [α] _D ²⁰ Solubility g. per l. | 5.0 g. per 300 cc. [α] _D ²⁰ Solubility g. per l. | 5.0 g. per 300 cc. [α] _D ²⁰ Solubility g. per l. | 10.0 g. per 300 cc. [α] _D ²⁰ Solubility g. per l. | 10.0 g. per 300 cc. [α] _D ²⁰ Solubility g. per l. | | |
| -204.2° | 11.66 | -0.13° | 0.084 ¹ | -0.12° | 0.163 | -0.14° | 0.163 | -0.14° | 0.163 | -0.16° | 0.323 |
| | | | 0.080 | | 0.163 | | 0.160 | | 0.310 | | 0.308 |
| | | | 0.085 | | 0.164 | | 0.165 | | 0.322 | | 0.320 |
| | | | 0.082 | | 0.163 | | 0.164 | | 0.313 | | 0.310 |
| | | Av. | 0.083 | Av. | 0.163 | Av. | 0.163 | Av. | 0.317 | Av. | 0.315 |
| -148.7° | 11.65 | -0.12° | 0.139 ¹ | -0.14° | 0.256 | -0.14° | 0.325 | -0.16° | 0.323 | | |
| | | | 0.148 | | 0.240 | | 0.310 | | 0.308 | | |
| | | | 0.144 | | 0.238 | | 0.322 | | 0.320 | | |
| | | | 0.144 | | 0.256 | | 0.313 | | 0.310 | | |
| | | Av. | 0.144 | Av. | 0.248 | Av. | 0.317 | Av. | 0.315 | | |
| -115.0° | 11.64 | -0.09° | 0.154 ² | -0.15° | 0.294 | -0.16° | 0.322 | -0.16° | 0.313 | | |
| | | | 0.150 | | 0.299 | | 0.308 | | 0.325 | | |
| | | | 0.154 | | 0.308 | | 0.310 | | Av. | | |
| | | | 0.154 | | 0.305 | | 0.320 | | 0.319 | | |
| | | Av. | 0.153 | Av. | 0.301 | Av. | 0.315 | Av. | 0.319 | | |

¹ Residue of hexagonal crystals in A² No detectable residue in A

TABLE II (Continued)

| [α] _D ²⁰ of sample | % N | TABLE II (Continued) | | | |
|---------------------------------------------|--------|---------------------------------------------------------------------------------|--------------------------------------------------------------------------------|--------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| | | A 0.05 g. per 300 cc. [α] _D ²⁰ Solubility per l. | B 0.5 g. per 300 cc. [α] _D ²⁰ Solubility per l. | C 5.0 g. per 300 cc. [α] _D ²⁰ Solubility per l. | D 10.0 g. per 300 cc. [α] _D ²⁰ Solubility per l. |
| 0° | 11.62 | | +0.12° 0.648 0.638 0.650 0.642 Av. 0.644 | +0.11° 0.625 0.635 0.630 0.625 Av. 0.629 | +0.12° 0.630 0.636 0.632 0.632 Av. 0.632 |
| +12.0° | 11.61 | | +0.21° 0.471 0.465 0.482 0.476 Av. 0.473 | +0.21° 0.563 0.556 0.558 0.561 Av. 0.560 | +0.20° 0.545 0.550 0.548 0.546 Av. 0.547 |
| -112.5° ^a | | | 0.455 0.455 0.449 0.453 Av. 0.453 | -0.11° 0.650 0.640 0.645 0.642 Av. 0.644 | +0.11° 0.661 0.664 0.651 0.668 Av. 0.661 |

^a Composite (dry) of 0° and -204.2° lots

the prevalent idea that these crystals represent the laevo form, with which even the "A" solution has been saturated. The -148.7° lot gives a much higher plateau, 0.115 gm. per liter but practically the same observed rotation. This increase in total solubility must be ascribed to the appearance of a new phase. The -115.0° lot gave the same plateau figure as the previous lot indicating that, although racemization had proceeded further no new phase had appeared. The inactive sample gave the highest value of all, 0.635 gm. per liter. The one dextro lot had a plateau figure which was slightly lower, 0.555 gm. per liter, indicating the absence of one of the phases which was present in the inactive sample. These figures obviously indicate an increase in solubility as optical activity decreases, such that increased proportions of solid to liquid are required to give plateau solubility figures. Even in the case of the sample of highest activity (-204.2°) there is evidently a very small proportion of an inactive phase which required more than the minimum ("A") proportion of solid to furnish enough for saturation.

In racemizing such a compound as cystine, containing two asymmetric carbon atoms of identical configuration, a situation is encountered analogous to that of tartaric acid. To racemize any sample, the configuration of some of the carbon atoms of some of the molecules must be reversed. It seems improbable and contrary to past experience that both asymmetric carbon atoms are affected simultaneously, forming the optical antipode at one step. On the other hand, if they are reversed one at a time, the only other alternative, the result can only be the formation of the meso form as an intermediate step in the racemization process, followed by later reversal of the group on the other asymmetric atom. Thus the sequence is: laevo to meso, meso to dextro, and depending on conditions, dextro plus laevo to racemic compound.

If the optical activity figures be temporarily neglected and the phases assumed to appear in this order: laevo, meso, dextro which unites with the excess laevo to form the dl compound, and finally a dextro phase, a rough idea of the solubility of each phase may be gained by the following method of reasoning.

The -204.2° lot is evidently not pure l-cystine but contains some other phase, most probably the meso. Because a constant rotation of about -0.13° was obtained with all samples of the -204.2° lot, the solutions must be, in all cases, saturated with the l-phase, and its solubility must be less than the lowest figure obtained. Therefore 0.083 gm. per liter may be taken as a maximum figure for the solubility of the laevo phase. Moreover, as stated above, a microscopic examination of the residue disclosed the presence of the hexagonal plates which commonly occur in the more laevo samples of cystine. The increase in total dissolved cystine from 0.083 to 0.163 gm. per liter may be attributed to saturation with the other phase present, probably the meso. As racemization progresses, it is found that a new plateau value is reached. The -148.7° and the -115.0° lots both give 0.315 gm. per liter as a saturation figure. This higher figure may be assumed to be due to the appearance of a new phase, which should be the dl compound, formed by the combination

of some of the newly formed dextro with some of the laevo. If then, the two plateau figures be subtracted, a solubility value for the third phase will be obtained.

$$\begin{array}{r} -115.0^\circ \\ -148.7^\circ \\ -204.3^\circ \end{array} \begin{array}{r} l + m + dl \\ l + m \\ \hline dl \end{array} \begin{array}{r} 0.315 \text{ gm. per l.} \\ 0.163 \text{ gm. per l.} \\ 0.152 \text{ gm. per l.} \end{array}$$

The inactive sample gave a still higher plateau figure and a water solution which was dextro rotatory. These facts suggest the appearance of a dextro phase, more soluble than the laevo. The difference in solubility value between this sample and the -115.0 lot should be due to the appearance of the dextro phase.

$$\begin{array}{r} 0.0^\circ \\ 115.0^\circ \end{array} \begin{array}{r} l + m + dl + d \\ l + m + dl \\ \hline d \end{array} \begin{array}{r} 0.630 \text{ gm. per l.} \\ 0.315 \text{ gm. per l.} \\ 0.320 \text{ gm. per l.} \end{array}$$

The $+12.0$ lot may be assumed to have no laevo phase present.

$$\begin{array}{r} 0.0^\circ \\ +12.0^\circ \end{array} \begin{array}{r} m + dl + d + l \\ m + dl + d \\ \hline l \end{array} \begin{array}{r} 0.630 \text{ gm. per l.} \\ 0.555 \text{ gm. per l.} \\ 0.075 \text{ gm. per l.} \end{array}$$

The solubility of the meso can be obtained from the first or -204.2° lot.

$$\begin{array}{r} -204.2^\circ \\ \\ \\ \end{array} \begin{array}{r} l + m \\ l \\ \hline m \end{array} \begin{array}{r} 0.163 \text{ gm. per l.} \\ 0.075 \text{ gm. per l.} \\ 0.088 \text{ gm. per l.} \end{array}$$

It should be noted that the figure of 0.075 g. per liter obtained above for the l-phase is very close to that obtained as a maximum value for its solubility in the A series of the -204.2° sample.

If the solution is saturated with one or more phases the addition of a sample containing other phases should cause increased solubility values, even though the rotation of the HCl solution of the total sample should be the same for some sample with fewer phases than the mixture. Thus the history of the sample should be considered when making solubility determinations. To test this point a mechanical mixture was made by grinding together in a mortar the proper proportions of the inactive and the -204.2° lots so as to give a rotation in HCl solution of -115.0° . The actual specific rotation obtained was -112.5° . This mixture should have all four phases present while the -115.0° sample, prepared by boiling a laevo sample with HCl, should have, according to the theory, only the l-, m-, and dl forms. The solubility value of the mixture was slightly higher (see Table II) than that obtained for the inactive, but showed no agreement with the -115.0° lot. It is evident that there was no interaction during the time available between the various phases present since otherwise the dextro-phase assumed to be present in the

inactive sample would have combined with the excess of laevo phase from the -204.2° lot, with the consequent removal of the dextro-and drop in solubility.

However, there should also be considered the possibilities of a readjustment of equilibrium conditions between the d- and l- forms and the dl-compound. Since racemic compounds are usually regarded as being dissociated in solution, the following equilibrium would obtain:



Such an equilibrium would produce the two antipodes in equimolecular proportions and an inactive solution would result provided that exterior influences react equally on the activities of both forms. If such an equilibrium as the above holds, the solubility of the dl-compound should be decreased by the presence of excess quantities of either antipode, particularly of the more soluble d- form. The resulting adjustments should then cause progressive solution of both d- and l- forms and removal as the dl- compound since the concentrations of both antipodes, indicated by their solubilities, are far in excess of that indicated by the "solubility product" of the dl- compound, as calculated from its solubility. The net result would be that a sample originally inactive in acid solution should produce only an inactive water solution since the inactive sample should contain equimolar amounts of both configurations, regardless of their form of combination, and the adjustment of the above described equilibrium results in the removal of equimolar proportions to form the dl-compound. Since the opposite is true, i.e., an inactive sample actually produces a dextro-rotatory water solution, it is to be inferred that no such adjustment takes place. We have shown by experiment that the dextro rotation persists at least for several weeks. That the inactive sample of cystine used for these determinations was really inactive seems fairly certain. It not only failed to show any detectable rotation under standard conditions but it also failed to show any when the concentration of the cystine and the acidity of the solution were both varied. Change in temperature also had no effect.

When we consider the optical activity figures certain discrepancies are seen. The values for the observed rotation of the solutions obtained from the laevorotatory samples indicate constant saturation with the laevo phase, although the steady upward drift of these values suggests a slight increase in solubility as the proportion of the inactive phase increases. However, if we similarly credit the dextro phase with being the cause of the rotation obtained from solutions of the $+1.20^\circ$ lot, it is evident that while solubility figures suggest that the dextro phase is four times as soluble as the laevo, the observed rotations are respectively about -0.13° and $+0.21^\circ$.

In the case of the inactive sample the dextro rotation observed could be explained by the difference in solubilities between the d- and l- phase, the $+0.12^\circ$ value being regarded as the algebraic sum of the rotation of the saturated d- and l- solutions. Assuming equal rotatory effects from equal

concentrations of each, this would argue a rotation of a water solution of d-form alone as about $+0.25^\circ$ or $+0.26^\circ$. The dextro sample actually gave a value of $+0.21^\circ$. The artificial mixture of $[\alpha]_D = -112.5^\circ$ shows about the same positive rotation as the inactive sample for the same reason.

The specific rotations of these isoelectric solutions are also of interest. The activities of the solutions in Table II are expressed in terms of observed rotation. In calculating the specific rotation only the concentration of the active phase and not the total solubility of the sample should be considered. By using the solubility figures for l- and d- cystine obtained above, it is found that l- cystine has a specific rotation of -433 and d- of $+164$. No explanation can at present be offered as to why these two antipodes differ in specific rotation. It can only be pointed out that the rotation of cystine solutions has been shown to be highly influenced by the presence of other substances and this influence may not necessarily be identical on the d- and l- forms. Such an influence may be exerted by the inactive phases. The above $[\alpha]_D$ value for l- cystine is, at this high dilution, approximately what one would expect from previously published curves of cystine rotations.⁽⁴⁾

The conclusion that the two enantiomorphs may have different solubilities is obviously highly unorthodox. While the possibility of some other explanation for the above results cannot be excluded it seems justifiable to expect much more experimental proof than exists at present in the literature before identical solubilities of such substances be regarded as a foregone conclusion. Of the many optical isomers known, exact solubilities have been determined for but a startlingly small number. Of these there are as many differences as identities recorded and the few identities concern substances of comparatively high solubilities such that slight differences—and one would expect such differences to be slight, if they exist at all—would be easily lost sight of.

Summary

The solubility of isoelectric cystine in water at 25°C was determined, using cystine samples of different specific rotations.

The existence is indicated of the following optical isomers of cystine: laevo, dextro, meso and racemic.

A solubility figure for each phase was calculated. The results suggest that the d- form may be about four times as soluble as the l-form.

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THE CATALYTIC DECOMPOSITION OF OLEIC ACID*

BY BARNARD M. MARKS WITH H. C. HOWARD, JR.

Introduction

This investigation grew out of an attempt to dehydrogenate sunflower seed oil and thus convert it into an oil possessing better drying qualities. Experiments on the hydrogenation of sunflower seed oil using a nickel catalyst were conducted in this laboratory with success by French and Humphrey¹. What are the possibilities of the reverse reaction? Several series of experiments by the method and with apparatus similar to that which will be described gave evidence of dehydrogenation, but it also became evident from the reaction products obtained that the dehydrogenation of sunflower seed oil presents a difficult problem which is complicated by the fact that the oil, composed as it is of a mixture of glycerides of oleic acid and related unsaturated acids, yields a very complex set of products when it undergoes decomposition in the presence of catalysts. A study of the action of catalysts on pure oleic acid therefore appeared to be a logical starting point.

While the literature² is replete with experiments on the hydrogenation of the unsaturated fatty acids as well as the glycerides, the reverse reaction has received but scant study. Mailhe³ did some work on various glycerides to form motor spirits. He used copper-magnesia or copper-alumina catalysts. Working at temperatures of 600° to 650°C he hydrogenated the more volatile components and obtained a yield of 20 to 30 per cent of a motor fuel consisting of a mixture of benzene, toluene, hexanes, and other hydrocarbons.

Bussy,⁴ Tilley,⁵ and Krafft⁶ studied the destructive distillation of castor oil. Stadnikov and Ivanovski⁷ found that the fatty acids obtained by the hydrolysis of linseed oil would be decomposed by an iron-iron oxide catalyst at a temperature of 400°C when a stream of hydrogen is passed thru the oil, yielding mainly hydrocarbons and carbon dioxide. The most recent work is that of Simons⁸ on the catalytic decomposition of triacetin and tripropionin. He made a complete analysis of the volatile products resulting from the action of a thorium oxide catalyst at temperatures ranging from 420° to 525°C.

* Abstract of a thesis presented in partial fulfillment of the requirements for the degree of Chemical Engineer, University of Missouri, 1927.

¹ H. E. French and H. O. Humphrey: University of Missouri Bull., 27, No. 7 (1926).

² Paul Sabatier: "Catalysts in Organic Chemistry," (1923).

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⁴ M. Bussy: Ann., 60, 246 (1848).

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⁷ G. L. Stadnikov and E. E. Ivanovski: Trans. Karpov Inst. Chem. (Moscow), 4, 175 (1925); C. A., 20, 2480 (1926).

⁸ F. Simons: J. Am. Chem. Soc., 48, 1991 (1926).

Experimental

By way of orientation some experiments were conducted with finely divided platinum as catalyst. Attention was first directed to the composition of the gaseous products resulting from the decomposition. Samples of 75 grams of c.p. oleic acid were heated to 375° in the presence of the catalyst and kept at this temperature until reaction had practically ceased. The gaseous products were collected and analyzed in a modified and improved Orsat apparatus.¹ At the same time the liquid distillate was collected. The composition of the gas mixture is given in Table I.

TABLE I
Oleic Acid—Catalyst, Colloidal Platinum.

| Sample | Vol. cc | Unsaturated Hydrocarbons % | CO ₂ % | O ₂ % | H ₂ % | CO% |
|--------|---------|----------------------------|-------------------|------------------|------------------|-------|
| 1 | 72.8 | 2.34 | 8.80 | 2.88 | 0.3 | 86.8 |
| 2 | 74.6 | 2.14 | 8.16 | 2.75 | 1.88 | 60.4* |
| 3 | 59.8 | — | 7.55 | 2.34 | 1.83 | 82.0 |

* This low value is probably due to an experimental error.

From the volatile liquid products capric acid separated as a solid. After filtering off the capric acid, cooling of the filtrate gave a semi-solid mass, but no separation could be made by filtering it. An attempt to separate the components by fractional distillation did not give promise of success. After the distillate had been separated into 17 fractions, the boiling range of each being 10°, it was found that in almost every fraction a partial solidification, like the original, took place on slight cooling. It was found, however, that a considerable portion,—about 35 per cent—boiled within the range of 310° to 314°C. This fraction was found to contain 60 per cent unsaponifiable material which was later identified as hydrocarbons.

To gain further insight into the course of the reaction some preliminary experiments were conducted with finely divided nickel as catalyst. A sample of oleic acid was placed in the reaction flask with 1 per cent nickel catalyst

TABLE II
Liquid Distillate—Nickel Catalyst; Temp. = 375°C. Run No. 12

| Time (hrs.) | Weight (g) | Volume (cc) | Specific Gravity | Time (hrs.) | Weight (g) | Volume (cc) | Specific Gravity |
|-------------|------------|-------------|------------------|-------------|------------|-------------|------------------|
| 0.5 | 1.078 | 1.308 | 0.826 | 5.0 | 3.122 | 3.593 | 0.870 |
| 1.0 | 10.433 | 11.795 | 0.890 | 6.0 | 3.227 | 3.363 | 0.837 |
| 1.5 | 7.809 | 8.929 | 0.875 | 6.5 | 1.170 | 1.498 | 0.784 |
| 2.0 | 7.655 | 8.707 | 0.875 | 7.0 | 0.809 | 1.222 | 0.663 |
| 2.5 | 6.235 | 7.140 | 0.875 | 7.5 | 0.751 | 1.140 | 0.660 |
| 3.0 | 7.418 | 8.567 | 0.867 | 8.5 | 0.579 | 0.841 | 0.690 |
| 3.5 | 6.385 | 7.416 | 0.860 | 10.0 | 0.500 | 0.770 | 0.650 |
| 4.0 | 8.283 | 9.533 | 0.867 | 11.5 | — | One drop | — |
| 4.5 | 6.382 | 7.496 | 0.855 | | | | |

¹ United States Bureau of Mines modification.

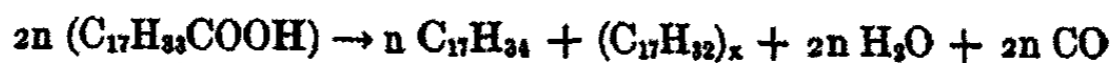
and kept at 375°C for 12 hours. The volatile liquid portion was collected in tared test tubes at half hour intervals. The gross weight of each sample was later determined and also its volume. The experimental data are given in Table II.

A graph of the total weight of distillate plotted against time shows a nearly linear function up to four hours and then gradually reaches a limiting value. The specific gravity of the distillate shows a rather abrupt decrease in the fractions obtained after 6.5 hours. About 70 per cent of the oleic acid was volatilized in 12 hours. No capric acid separated out in the distillate.

With these preliminary results in hand as well as the results of more extended experiments conducted with sunflower seed oil, a total of 13 trials, it was decided to make a systematic study of the catalytic action of nickel on oleic acid, since the nickel catalyst gave promise of furnishing the most information about the course of the reaction. The experiments include (1) ten runs made at chosen temperature intervals within the range of 200° to 400°C; (2) analysis of the gaseous products during the progress of the reaction; (3) determination of the following physical and chemical constants on the various fractions of the liquid distillate; the saponification equivalent, refractive index, per cent saponifiable, molecular weight, and iodine number; (4) fractionation of the residue left in the reaction flask under greatly reduced pressure, and determination on each fraction of the above physical and chemical characteristics.

The experimental results obtained, when considered collectively, clearly indicate that finely divided nickel exercises a specific catalytic effect on the decomposition of oleic acid which is quite distinct from the thermal decomposition which occurs simultaneously but relatively slowly. The results find a satisfactory explanation if it is assumed that the decomposition products obtained represent a combination of a specific catalytic and a thermal effect.

It is known¹ that oleic acid will decompose slightly on distillation at atmospheric pressures giving carbon dioxide, lower acids, and hydrocarbons. In the experiments it was found that in the presence of the catalytically active nickel that decomposition begins at temperatures as low as 200°C. The specific action of nickel is also shown by the fact that the main gaseous product is carbon monoxide.^{2,3} The volume of carbon monoxide was always found to be many times the dioxide. The stoichiometrical relations between the quantities of water, gases, distillate, and residue show that the catalytic activity of nickel under the conditions of the experiment should be regarded as a decarboxylation. The following mechanism is postulated for the predominating reaction:



Nearly all the experiments were conducted in the following manner: A sample of oleic acid weighing 75 grams was placed in the reaction flask,

¹ Allen: "Commercial Organic Analysis," 2, 403 (1910).

² G. Dougherty: J. Am. Chem. Soc., 50, 571 (1928).

³ P. Sabatier and Senderens: Ann. Chim. Phys., (8) 4, 467 (1905).

Fig. 1, with 1% active catalyst.¹ The flask was then sealed to the system. The air and occluded gases were next removed by means of an oil pump and then the flask and contents heated to the desired temperature. The temperature was maintained constant by the use of an electric heating unit. At the higher temperature, where the distillation of unchanged acid might be excessive, pure nitrogen was introduced and the pressure of the nitrogen increased to about 1.3 atmospheres. (See Table III).

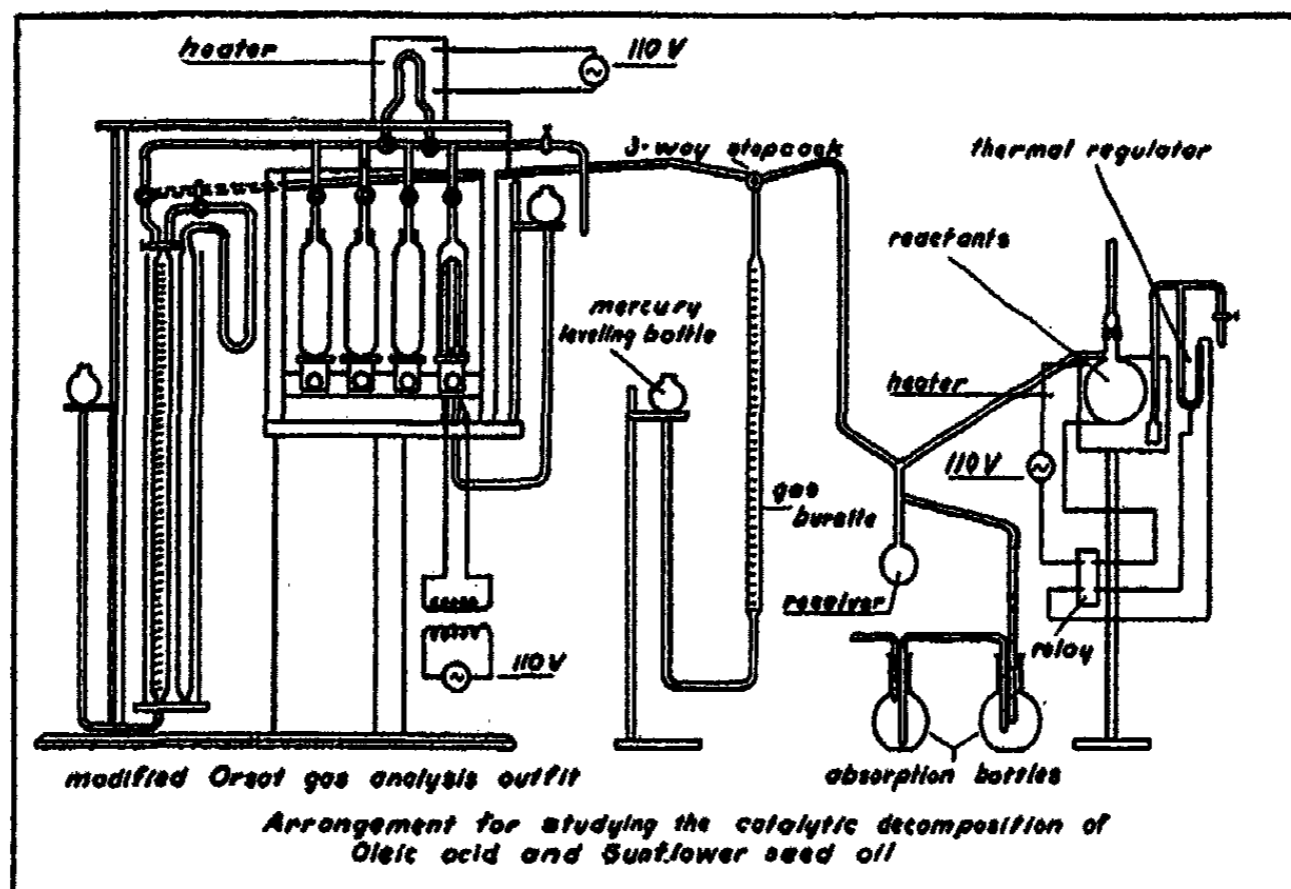


FIG. 1

In the runs made at the lower temperatures the gases were evolved so slowly that all of them could be analyzed at the time they were produced, but in later runs, at higher temperatures, the time required to complete the reaction becomes so short that only a few analyses could be made in each experimental run. In these experiments the total amount of gases was determined to ascertain whether any stoichiometrical relation exists between the gases evolved and the other products of the reaction obtained in the same experiment.

A water layer collected at the bottom of the receiver. This was separated from the layer of oil by means of a separatory funnel and weighed.

No way of separating the components in the oil layer of the distillate or in the residue left in the reaction flask was found. The percent saponifiable

¹ The nickel catalyst was prepared by treating a solution of nickelous nitrate with ammonium carbonate. The precipitated carbonate was heated in a muffle to convert it into the black oxide. The black oxide was then heated in a stream of hydrogen for 50 hours at 205°C. The nickel was found to have a peculiar green appearance which suggested the presence of some lower oxide of nickel. As the action of hydrogen seemed to be ineffective in reducing it further, the temperature was raised to 235°C. After an additional 16 hours, the product was a grey-black, finely divided, catalytic nickel.

was obtained by finding the average molecular weight of the soaps, and the total amount of titratable acidity. The molecular weight of the acids, which appear in the distillate, was found by precipitating as lead soaps directly from alcohol solution by means of a saturated solution of lead perchlorate in 95 per cent alcohol. The soaps precipitated almost immediately in 15 to 20 volumes of alcohol solution. After filtration of the precipitated soaps and removal of alcohol in a vacuum desiccator, the dried soaps were analyzed for lead by the standard sulfate method.¹ The molecular weight of the saponifiable portions was also determined by direct titration of the fatty acids with a standard base².

In experiments on the solubility of the distillate it was found that a portion was insoluble in twice its volume of 95% alcohol, and this part proved to be unsaponifiable.

The product that was separated by its insolubility in 95 per cent alcohol was colorless and remained colorless while the original distillate changed from a colorless to a light yellow oil. The product obtained as unsaponifiable by the standard separation was colored. The physical constants of each were determined and very slight differences were found. The volatile products which condensed at room temperatures were thus divided into three parts: (1) The water layer; (2) a saponifiable portion containing the unchanged oleic acid and other acids, which were determined in two ways, (a) by precipitation of lead soaps and (b) by direct titration; (3) an unsaponifiable portion separated (a) by its insolubility in alcohol, and (b) by the standard method.

The residues that remained behind in the reaction flask were also subjected to analysis. A small portion was first removed as a sample for analysis. It also served as a standard for comparison with the distilled portions into which the residue was separated. The residues were fractionated by high vacuum distillation under a pressure of 5 mm or less. The receiver was sealed to the distilling flask by means of a long piece of glass tubing which served as a condenser. Three fractions were taken. The first was obtained by regulating the temperature to 200°C and allowing what would distill to accumulate. It took about 24 hours to complete this distillation. When it was found that no further distillation occurred at 200°C, the receiver was changed and the temperature raised to 300°C. The same procedure was followed at this temperature and then the last fraction was collected at a temperature of 440°C. There remained a dark lustrous residue adhering to the sides of the hot reaction flask, which on cooling contracted and broke into many small pieces. The distillates were all slightly colored and showed a yellow-green fluorescence. The color was observed to be darker in the portions that distilled at the higher temperatures.

¹ W. W. Scott: "Standard Methods of Chemical Analyses," 274.

² The fatty acids referred to were separated from the distillate by addition of an excess of potassium hydroxide solution. The hydrocarbons present were extracted with ether. The aqueous layer containing the soaps was then acidified with sulfuric acid, and the free fatty acids were extracted with ether. After evaporation of the ether, a weighed sample of the free fatty acids was dissolved in alcohol and titrated directly with standard base.

The data obtained from ten runs is given in tabulated form. In Table III are recorded the temperature range of each run, period of reaction, operating pressures, runs in which pure nitrogen was present initially in the reaction flask, percentage of volatile products formed in the course of the experiment, the equivalent weight of distillate, and the total volume of gas evolved, measured at 20°C.

TABLE III
Decomposition of Oleic Acid, Catalyst, 1% Nickel.

| Run No. | Temp. Range | Period (hrs.) | Pressure mm | Foreign Gas | Volatile % | Equiv. Wt. of Distil. | Vol. Gas cc |
|---------|-------------|---------------|-------------|----------------|------------|-----------------------|-------------|
| 14 | 235-240 | 72 | 0-760 | | 12.94 | 935 | — |
| 15 | 245-250 | 96 | 760 | | 27.40 | 820 | — |
| 16 | 290-310 | 96 | 0-760 | | 33.80 | 830 | — |
| 18 | 319-357 | 12 | 760 | N ₂ | 43.7 | 981 | — |
| 17 | 330-370 | 96 | 0-760 | | 44.5 | 983 | — |
| 21 | 345-390 | 3.5 | 1000 | N ₂ | 44.50 | 679 | 5251 |
| 19 | 375-420 | — | 760 | N ₂ | 45.60 | 1083 | — |
| 22 | 380-440 | 4.5 | 1000 | N ₂ | 50.45 | 696 | 5310 |
| 20 | 400-475 | — | 760 | N ₂ | 52.60 | 521 | 3000 |
| 23 | 420-490 | 2.5 | 1000 | N ₂ | 58.00 | 600 | 4550 |

It was found that at higher temperatures there was a tendency for unsaturated gaseous hydrocarbons to be formed, which was not observed at the lower temperatures where the mixture of hydrocarbons as gases consisted largely of methane. In run #15 the gas mixture contained 5.78% saturated hydrocarbons. The volume composition of the gas mixtures obtained in the several runs is given in Table IV, which includes in addition the per cent of water which each sample of acid yielded.

TABLE IV
Composition of Evolved Gases

| Run | % CO | % H ₂ | % O ₂ | % CO ₂ | % Unsaturation | % H ₂ O |
|-----|-------|------------------|------------------|-------------------|----------------|--------------------|
| 14 | 74.50 | 1.82 | 3.73 | 9.27 | — | 4.00 |
| 15 | 81.29 | 2.93 | 1.37 | 13.71 | — | 2.93 |
| 16 | 82.48 | 2.71 | 2.44 | 9.70 | 2.42 | 5.34 |
| 17 | 84.21 | 3.65 | 0.41 | 8.32 | 2.51 | 4.54 |
| 18 | 84.55 | 3.36 | 1.20 | 9.53 | 2.48 | 5.85 |
| 19 | 78.00 | 2.26 | 2.92 | 14.50 | 2.92 | 5.64 |
| 20* | 55.40 | 16.20 | 6.18 | 7.28 | 8.70 | 2.66 |
| 21 | 82.50 | 3.43 | 1.66 | 6.42 | 2.63 | 4.27 |
| 22 | 86.00 | 3.78 | 1.50 | 6.19 | 2.29 | 4.54 |
| 23 | 84.10 | 4.56 | 0.14 | 6.97 | 4.73 | 4.60 |

* The composition of the gases in run No. 20 is abnormal, probably as a result of analytical errors.

An example will show how the stoichiometrical relations given in Table V were computed from data recorded in Tables III and IV. In run #22, the total volume of gas evolved measured 5310 cc. at 20°C, 760 mm. pressure. The carbon monoxide in the gases evolved equals 0.915 mole. The actual amount of water collected was 3.405 g or 0.189 mole. The equivalent weight of the distillate was found to be 696 and since its weight was 37.84 g, there is present in it 0.055 mole of acid which we may assume to be oleic acid which distilled over during the run. The amount of carbon dioxide obtained was 0.014 mole, and if we assume that this resulted from the thermal decomposition of oleic acid, then to find the amount of acid decomposed catalytically we deduct from the original charge of 0.265 mole (75g), of oleic acid both of these values, thus leaving 0.196 mole. On the basis of these relations the equation on page 1042 was formulated.

TABLE V
Some Quantitative Relations

| Run No. | Moles Oleic Acid decomposed catalytically | Moles CO formed | Moles Water formed | Moles CO / Moles H ₂ O |
|---------|-------------------------------------------|-----------------|--------------------|-----------------------------------|
| 21 | 0.201 | 0.189 | 0.192 | 0.984 |
| 22 | 0.196 | 0.195 | 0.189 | 1.036 |
| 23 | 0.179 | 0.160 | 0.177 | .902 |

Since the molecular ratios of acid and water and carbon monoxide deviate somewhat from unity it is probable that the reaction mechanism is more complex than that represented by the simple equation which we have postulated. The presence in the gases evolved of hydrogen, oxygen, and unsaturated hydrocarbons likewise indicates side reactions. The carbon dioxide in the gas mixture may in the main be the result of thermal decomposition. Unfortunately the importance of the total gas volume was not recognized in the early runs.

In each run the index of refraction was measured on seven liquid products namely, the oily layer of the distillate, the residue in the reaction flask, the three fractions into which the original residue was fractionated, the unsaponifiable liquid separated by the standard method, and the unsaponifiable portion obtained by direct separation with alcohol. The variations in the values of the refractive index of the different liquids over the entire series of experiments are very small indeed, lying between 1.446 and 1.4564, oleic acid itself having the index 1.460

Iodine Numbers. The iodine numbers here reported represent the average of two determinations. The condensed data are given in the following Table VI. The run numbers are arranged in the order of temperature. The iodine value of oleic acid is 90.

The iodine numbers apparently are rather fluctuating but at a temperature of about 300° the values show a minimum of 74 for each portion of the distillate as well as residue.

TABLE VI
Iodine Numbers

| Sample | Run 14 | 15 | 16 | 18 | 17 | 21 | 19 | 22 | 20 | 23 |
|------------------------------|--------|-------|------|------|------|------|------|------|------|------|
| Distillate | 80.6 | — | 75.2 | 85.0 | 96.8 | 80.5 | 88 | 88.5 | 87 | — |
| Residue | 90.7 | 79.9 | 73.7 | 77.1 | 85.1 | 82.3 | 74.3 | 80.9 | 77.9 | 79.1 |
| Residue 200° fractionated | — | 90.8 | 73.0 | 71.4 | 78.0 | 80.3 | 63.7 | 77.0 | — | — |
| Residue 300° fractionated | 81.9 | 94.2 | 53.5 | 70.8 | 74.5 | 67.9 | 57.7 | 74.6 | 69.4 | — |
| Residue 440° fractionated | — | 65.5 | 77.7 | 69.0 | 67.4 | 71.0 | 74.7 | 82.5 | 75.6 | 59.8 |
| Unsaponifiable (Std.) | — | 99.2 | 73.8 | 84.5 | 73.8 | 93.6 | 82.0 | — | 92.5 | 75.7 |
| Unsaponifiable (direct) | 88.8 | 103.1 | 74.6 | 93.3 | 74.6 | 93.0 | 89.6 | 93.1 | 85.8 | — |

The molecular weights of the several portions were determined by the freezing point lowering in benzene as solvent. The molecular weight of oleic acid in benzene was found to be 526, while the formula weight is 282. The molecular weight of benzoic acid was found to be 235 in benzene. The molecular depression constant of benzene was assumed to be 50.0

TABLE VII
Molecular Weights

| Sample | Run 14 | 15 | 16 | 18 | 17 | 21 | 19 | 22 | 20 | 23 |
|----------------------------|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Distillate | 249 | 249 | 224 | 254 | 253 | 274 | 241 | 303 | 287 | 337 |
| Residue* | 738 | 674 | 610 | 667 | 687 | 721 | 686 | 712 | 647 | 583 |
| Residue, 200° fraction | — | 245 | 236 | 256 | 291 | 334 | 248 | 340 | 260 | — |
| Residue, 300° | 246 | 225 | 348 | 402 | 485 | 412 | 245 | 409 | 350 | 399 |
| Residue 440° | — | 242 | 716 | 216 | 347 | 372 | 291 | 320 | 331 | 380 |
| Unsaponifiable (Std) | — | 240 | 227 | 218 | 227 | 281 | 258 | 231 | 250 | — |
| Unsaponifiable (direct) | 244 | 214 | 240 | 241 | 240 | 232 | 211 | 239 | 214 | — |

* The residue in the reaction flask was found to be completely soluble in ether.

The high molecular weight of the residue left in the reaction flask indicates that polymerization products are formed, which on distillation in vacuo, decompose into compounds of lower molecular weight as indicated by the lower values for each fraction. The molecular weights of the unsaponifiable portion of the distillate have an average value in good agreement with the molecular weight and iodine number of an unsaturated hydrocarbon $C_{17}H_{34}$.

The percentage of nonsaponifiable products averaged about 60 per cent in the different runs, and appeared to be independent of the temperature at which the reaction took place.

Summary

The catalytic activity of nickel toward oleic acid has been studied through the temperature range of 200°C to 490°C.

Analytical data are given for the different products of the reaction.

The decarboxylating catalysis of nickel has been demonstrated for oleic acid.

Oleic acid was found to give mainly carbon monoxide, water and hydrocarbons on catalytic decomposition.

An explanation of the observed data is given; and an equation for the mechanism of the main reaction is proposed.

*Chemical Laboratory,
University of Missouri,
1927.*

THE LATENT HEAT OF FUSION OF NAPHTHALENE FROM NEW SOLUBILITY DATA*

BY ARTHUR A. SUNIER AND CHARLES ROSENBLUM

The method of Hildebrand and Jenks¹ for evaluating solubility data has been applied by Mortimer² to binary solutions involving non-polar and in several instances even polar components. The method consists in plotting the logarithm of the mol fraction of solute against the reciprocal of the absolute solubility temperature. From the ideal solubility equation

$$\text{Log } N = - \frac{L}{4.58 T} + I$$

where L is the molal latent heat of fusion of solute, N the mol fraction of solute, T the absolute solubility temperature, and I a constant of integration, it follows that for an ideal solution, the curve obtained is a straight line

the slope of which is given by $S = \frac{\text{Log } N}{1/T}$. For most solutions involving

non-polar components, a fairly representative straight line can be drawn through the points corresponding to higher concentrations of solute, and a slope obtained.

If substances of distinctly non-polar nature are used, assuming that no molecular changes take place in solution, the slopes are indicative of the relative internal pressures of solvents concerned. Mortimer has constructed a nomograph with a great many compounds arranged according to their relative internal pressures and finds that by employing factors representing the ratio between experimental slopes and the ideal, he can predict the solubility of these substances in one another with a fair degree of accuracy.

As the basis for relative internal pressure comparison Mortimer uses that of naphthalene, which gives an ideal slope of 970 as calculated from the value 34.69 calories per gram given by Bogojawlenski³ for the heat of fusion at its melting point. The more recent work of Andrews, Lynn, and Johnston⁴ on the latent heat of fusion of organic compounds indicates a somewhat higher ideal slope of 990 for naphthalene. However, Ward,⁵ who has made an extended investigation of the solubility relations of naphthalene, has obtained a slope of 970 from the upper portion of the $\text{Log } N$ versus $1/T$ curve for the system naphthalene-chlorobenzene which appears to be approximately ideal.

* Contribution from the Chemical Laboratory of the University of Rochester.

¹ J. Am. Chem. Soc., 42, 2180 (1920).

² J. Am. Chem. Soc., 44, 1416 (1922); 45, 633 (1923).

³ Chem. Zentr., (5) 9 II, 945 (1905).

⁴ J. Am. Chem. Soc., 48, 1274 (1926).

⁵ J. Phys. Chem., 30, 1316 (1926).

It seems likely that a study of solutions which do not deviate greatly from the ideal would throw light upon the magnitude of the heat of fusion of naphthalene. Mortimer¹ has calculated, apparently from freezing point data, the slopes of the Log N versus $1/T$ curves for naphthalene in ethylene chloride and bromide, and finds those solutions almost ideal. Accordingly the solubility of naphthalene in these solvents as well as in the corresponding ethylidene compounds has been determined in an effort to obtain a more definite indication of the latent heat of fusion of naphthalene from solubility data.

Experimental

The synthetic method of Alexejew² has been employed in making the solubility determinations recorded. The method is essentially the heating of weighed quantities of solute and solvent in a sealed tube and noting the highest temperature at which but few small crystals of solute remain in equilibrium with solution. Precautions assuring the attainment of equilibrium at the solubility temperature have been described by Ward. A bath of four liter capacity, a heating rate of not more than a hundredth of a degree per minute, and rotation of the sealed tube by motor were found to give satisfactory results. Uniformly small crystals were first obtained by heating to above the solubility point and rapidly cooling. The maximum error in the solubility temperature is estimated by Ward to be not more than three tenths of a degree.

Ward's procedure, except for certain modifications, has been used in this investigation. The water bath was heated by means of Cenco lagless heaters or Hotpoint immersion heaters in series with resistance sufficient to cut out all current if so desired. The resistances allowed accurate control of the rate of temperature increase.

The procedure in heating was somewhat modified. Instead of heating at a uniformly slow rate, an attempt was made to approximate conditions of the so-called equilibrium method of determining solubility. The temperature was raised rapidly to within several degrees of the solubility temperature, then more slowly at about a tenth of a degree per minute to within three or four tenths of a degree from the solubility point which can be approximated from the general appearance and quantity of crystals in the tube. The bath temperature was then kept constant at each tenth of a degree for about an hour till the solubility point was reached. The recorded solubility temperature was the highest temperature at which a very small quantity (several small crystals) of solute remained in equilibrium with solution. Immediately upon recording the solubility temperature, the bath was cooled at a rate of about 0.05 degree per minute. In all determinations recorded, marked increase in size of the crystals was noted within 0.1° to 0.2°. This is important as an indication that super saturation did not take place and that the solubility temperature as noted represents equilibrium conditions. Beckmann

¹ J. Am. Chem. Soc., 44, 1416 (1922).

² Wied. Ann., 28, 305 (1886).

thermometers were used to check the rate of increase and the constancy of the bath temperature. This modification in heating procedure was made in an effort to overcome the error introduced by differences in the size of crystals.

Pyrex glass tubing of 7-9 mm. inside diameter and a half millimeter or less thick was used for the solubility tubes. The heating procedure tends to overcome the difficulty raised by the time required for the solution to attain thermal equilibrium with the bath through the glass wall.

In making up the solubility tubes an attempt was made to restrict the vapor space to a very small volume. For tubes containing low naphthalene concentrations, it was found advisable to add the solvent first. The solid component formed a sort of protective layer preventing excessive evaporation of solvent and allowing the tube to be sealed closer to the surface of the material. For higher naphthalene concentrations the solute was added first, the greater part of it being fused in the tube by immersion in a water bath between 85 and 90° C. The fusion was carried out with the solubility tube inside a stoppered eight inch test tube to prevent absorption of water vapor.

Uniform bath temperature was insured by a twelve inch Cenco turbine stirrer (1000 R.P.M.). The contents of the solubility tube were shaken by attaching the tube to a cross-piece one end of which was alternately raised and lowered by an eccentric motion. It was found the bubble of vapor moving from one end of the tube to the other agitated the crystals of solute sufficiently.

The bath was surrounded by a wooden casing lined with asbestos pads to prevent any cooling effect from drafts.

The accuracy of the method was checked by repeating some of Ward's work on benzene. The benzene was purified partially according to the method of Richards and Shipley¹ except that no recrystallizations of solid benzene were attempted and distillation was carried out over phosphorus pentoxide. It was found that Ward's data could be checked within the error estimated for the method. Some of the work on naphthalene-ethylene chloride was repeated using somewhat poorer materials. The deviation was well within the three-tenths of a degree limit.

Some preliminary experiments on more rapid heating rates were carried out. It was found that heating as rapidly as a tenth of a degree per minute when approaching the solubility temperature occasioned only seldom an error of three-tenths of a degree.

Measurements were not carried below room temperature since, as Ward has pointed out, deviations from even an approximate straight line relationship are always greater at lower temperature.

The thermometers used were compared with a thermometer recently standardized by the Bureau of Standards. It is believed that temperature measurements were never in error as much as ± 0.07

¹ J. Am. Chem. Soc., 36, 1825 (1914).

Materials

All materials used were obtained from the Eastman Kodak Company. Two samples of naphthalene were used in the determinations. Both were purified by recrystallization from methyl alcohol dried over calcium oxide and distilled. A small quantity of sample A was recrystallized thirteen times making small cuts, whereas a large amount of sample B was recrystallized eight times making very large cuts in the amount of solid crystallizing out. Both samples were used interchangeably in some of the determinations without any apparent deviation from the temperature versus concentration curves.

The purity of the naphthalene was tested by taking its melting point according to the method of the Bureau of Standards.¹ The final fraction of sample A held over one tenth of a degree for more than forty minutes using an ordinary thermometer graduated to degrees. The fraction of sample B tested (after five recrystallizations) gave a melting point of 80.10° to 80.12° using the prescribed naphthalene thermometer obtained from the Taylor Instrument Company.

No attempt was made to purify excessively any of the solvents used other than by fractional distillation through a Clarke-Rahrs column. Cohen² has shown that the solubility of anthracene is little influenced by traces of moisture. The same probably holds for naphthalene, a very similar compound. Each solvent was twice distilled and representative fractions from the second distillations were used in the final determinations. Preliminary work with ethylene chloride only once distilled showed no deviations from the final results herein recorded.

The corrected boiling points of the solvents used are:—

| | |
|-----------------------------------------|-----------------------|
| Ethylene chloride | 83.43 to 83.48 C. |
| Ethylene bromide ³ | 131.1 (131.5) (131.7) |
| Ethylidene chloride | 57.3 to 57.4 |
| Ethylidene bromide | 106.8 to 107.0 |

Results

The experimental results have been incorporated in Tables I-IV. Table V contains the solubility of naphthalene in all four solvents at rounded temperature. All experimentally determined points have been plotted in Figs. 1 and 2. As is apparent from the figures, the points are too close together to allow individual curves to be drawn for each solvent on so small a scale.

¹ Sci. Paper Bur. Standards, No. 340.

² Z. physik. Chem., 119, 247 (1926).

³ At the conclusion of the solubility work on ethylene bromide it was found that Timmerman and Martin (*J. Chim. phys.*, 23, 747 (1926)) found that its boiling point was 131.7°, when determined with great care. After some time it was found that the Anschutz thermometer (used only for the boiling point of ethylene bromide and ethylidene bromide) was unreliable to the extent of 0.4 to 0.6°. Two other samples of ethylene bromide were prepared; their boiling points, determined with great care, are given in the parentheses. Five new solubility tubes were made up with these two new fractions, and the solubility temperatures determined in the usual manner; four tubes were on the average only 0.1° low, which is very satisfactory agreement. It seems certain, therefore, that all three fractions of ethylene bromide were quite pure, but the recorded boiling point of the first is in error.

TABLE I
Solubility of Naphthalene in Ethylene Chloride

| Grams $C_{10}H_8$ | Grams $C_2H_4Cl_2$ | Mol Fraction $C_{10}H_8$ | Solubility Temperature |
|----------------------|-----------------------|-----------------------------|---------------------------|
| 2.386 | 0.164 | 0.918 | 75.7°C |
| 2.093 | 0.340 | 0.827 | 69.7 |
| 2.527 | 0.931 | 0.678 | 59.4 |
| 2.137 | 1.236 | 0.572 | 51.1 |
| 1.966 | 1.433 | 0.515 | 46.1 |
| 1.627 | 1.748 | 0.419 | 36.5 |
| 1.193 | 1.821 | 0.336 | 27.2 |

TABLE II
Solubility of Naphthalene in Ethylene Bromide

| Grams $C_{10}H_8$ | Grams $C_2H_4Br_2$ | Mol Fraction $C_{10}H_8$ | Solubility Temperature |
|----------------------|-----------------------|-----------------------------|---------------------------|
| 2.213 | 0.184 | 0.946 | 76.8°C |
| 2.804 | 0.966 | 0.810 | 68.9 |
| 2.051 | 1.259 | 0.705 | 61.7 |
| 1.899 | 1.740 | 0.616 | 55.1 |
| 1.325 | 2.062 | 0.485 | 44.4 |
| 1.103 | 2.515 | 0.392 | 35.3 |
| 1.065 | 4.287 | 0.268 | 20.7 |

TABLE III
Solubility of Naphthalene in Ethylidene Chloride

| Grams $C_{10}H_8$ | Grams CH_2CHCl_2 | Mol Fraction $C_{10}H_8$ | Solubility Temperature |
|----------------------|-----------------------|-----------------------------|---------------------------|
| 2.637 | 0.180 | 0.919 | 75.6°C |
| 2.402 | 0.396 | 0.824 | 69.8 |
| 1.938 | 0.612 | 0.710 | 62.6 |
| 1.800 | 0.737 | 0.654 | 58.6 |
| 2.081 | 1.291 | 0.555 | 50.8 |
| 1.320 | 1.152 | 0.470 | 43.3 |
| 1.259 | 1.629 | 0.374 | 33.0 |

TABLE III
Solubility of Naphthalene in Ethylidene Bromide

| Grams $C_{10}H_8$ | Grams CH_2CHBr_2 | Mol Fraction $C_{10}H_8$ | Solubility Temperature |
|----------------------|-----------------------|-----------------------------|---------------------------|
| 2.231 | 0.370 | 0.898 | 74.3°C |
| 1.539 | 0.540 | 0.807 | 68.5 |
| 1.948 | 1.082 | 0.726 | 63.0 |
| 2.063 | 1.972 | 0.606 | 53.7 |
| 2.063 | 2.535 | 0.545 | 48.4 |
| 1.189 | 1.772 | 0.496 | 44.1 |
| 1.016 | 3.239 | 0.315 | 23.9 |

TABLE V
Solubility of Naphthalene at Rounded Temperatures expressed as Mol Fraction Naphthalene

| Temperature | C ₂ H ₄ Cl ₂ | CH ₂ CHBr ₂ | C ₂ H ₄ Br ₂ | CH ₂ CHCl ₂ |
|-------------|-----------------------------------------------|-----------------------------------|-----------------------------------------------|-----------------------------------|
| 75°C | 0.911 | 0.910 | 0.910 | 0.909 |
| 70 | 0.831 | 0.830 | 0.828 | 0.825 |
| 65 | 0.756 | 0.755 | 0.752 | 0.745 |
| 60 | 0.686 | 0.685 | 0.682 | 0.674 |
| 55 | 0.620 | 0.621 | 0.615 | 0.608 |
| 50 | 0.560 | 0.562 | 0.552 | 0.545 |
| 45 | 0.503 | 0.506 | 0.493 | 0.488 |
| 40 | 0.452 | 0.456 | 0.439 | 0.437 |
| 35 | 0.405 | 0.409 | 0.389 | 0.391 |
| 30 | 0.360 | 0.366 | 0.344 | (0.350) |
| 25 | (0.318) | 0.324 | 0.302 | |
| 20 | | (0.286) | (0.262) | |

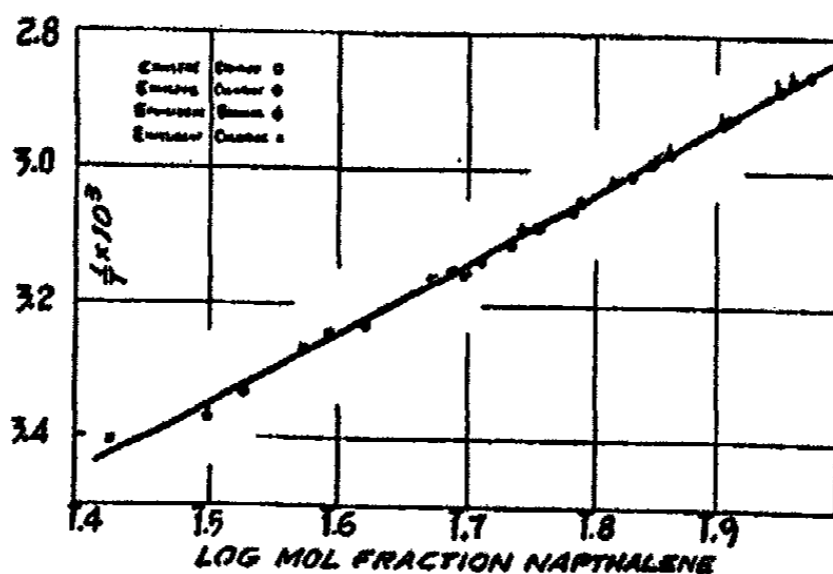


FIG. 1

Discussion

As has been pointed out, the slope of the straight line obtained by plotting the Log N versus $1/T$ curve for an ideal solution is given by $S = L/4.58T$. For solutions of non-polar components deviations from this slope are indicative of the relative internal pressure of solvent. For solutions which approach the ideal, the upper portion of the Log N versus $1/T$ curve should be a straight line with a slope related to the latent heat of fusion of solute.

For the solutions herein investigated, Table VI contains the slopes indicating heat of fusion of naphthalene and the range through which the straight line function holds.

The table seems to indicate that the lower value for the latent heat of fusion of naphthalene is the more likely. Except for the case of ethylene dichloride, which gives a slope somewhat less than 970, the solutions in ques-

tion appear to support Ward's¹ value for the slope of the Log N versus $1/T$ curve for naphthalene. The somewhat lower slope given by ethylene chloride² may possibly be explained on the grounds of slight solvation, as Hildebrand and Jenks³ account for the similar case of naphthalene in chloroform.

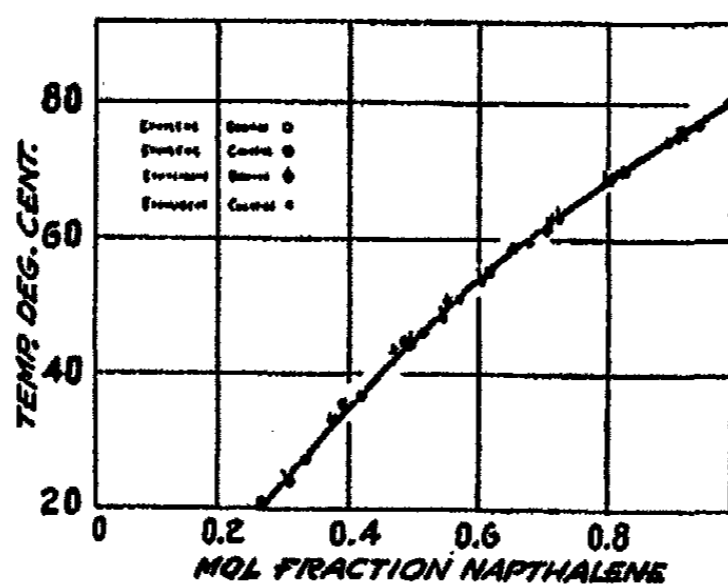


FIG. 2

TABLE VI

| Solvent | Experimental Slope | Calculated Lt of $C_{10}H_8$ | Lower Limit of Straight Line Function |
|--------------|--------------------|------------------------------|---------------------------------------|
| $C_2H_4Cl_2$ | 960 | 4400 cal. | $50^\circ C$ |
| CH_2CHBr_2 | 970 | 4440 | 60 |
| $C_2H_4Br_2$ | 975 | 4460 | 50 |
| CH_2CHCl_2 | 975 | 4460 | 65 |

Summary

1. The solubility of naphthalene in ethylene chloride, ethylene bromide, ethylidene chloride and ethylidene bromide has been determined.
2. The slopes of the upper portion of the log N versus $1/T$ curves have been calculated.
3. The data seems to indicate the value 4440 calories for the molal latent heat of fusion of naphthalene.

¹ J. Phys. Chem., 30, 1316 (1926).

² Hildebrand ("Solubility," 155 (1924)) gives a log N versus $1/T$ curve for naphthalene in ethylene chloride; the slope of the curve is almost the same as ours, as nearly as can be judged from the small figure. It is stated that Ward has supplied the data but thus far we have seen no published data on this system.

³ J. Am. Chem. Soc., 42, 2180 (1920).

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THE PREPARATION OF THE HYDROGEN ELECTRODE AND THE REMOVAL OF A COMMON SOURCE OF TROUBLE IN CONNECTION WITH ITS USE

BY STEPHEN POPOFF, ADOLF H. KUNZ, AND R. D. SNOW

Although an infinite amount of literature has been written about hydrogen ion determination by electrometric methods, very little can be found about the actual details of manipulation, methods of plating, factors affecting equilibrium, etc. That which has been published is often contradictory.

After describing the plating of electrodes Clark¹ frankly states, "It must be admitted that the above description is loose. This is because the rush of experimental application has prevented a detailed examination of conditions and experience has taught details difficult to formulate in exact language."

Ellis² maintains that the use of lead in platinizing solution is objectionable. On the other hand, Beans and Hammett³ have no difficulty in preparing platinized electrodes of high activity from solutions containing lead. Lewis, Brighton and Sebastian⁴ find a gold or gold plated electrode superior but Beans and Hammett do not find gold plating an advantage. Ellis prescribes platinizing until the coating is thick enough to shake off; Clark until the electrode is covered with a deposit of thickness sufficient to cover the glint of polished metal and so that it adheres under a vigorous stream of water; Tolman and Ferguson,⁵ till the electrode assumes a velvety appearance.

Similarly, authors are not agreed upon the time required for the electrodes to come to equilibrium and other details in electrometric determinations. In view of this lack of agreement and lack of information it seemed desirable to study the conditions and thereby obviate some of the difficulties.

Very often in electrometric determinations involving the use of the hydrogen electrode a poisoning of the platinum causes a decrease in potential which may even result in a reversal of polarity. This necessitates the replatinizing of electrodes, an expensive and time-consuming process. Therefore, it seemed desirable to devise some means of restoring the potential without replatinizing.

In this work a precision of ± 0.1 millivolt was sought. In an investigation on oxidation potentials in which the temperature was kept constant to $\pm 0.01^\circ$, duplicate electrodes prepared by the method given showed a maximum variation of 0.01 mv.

¹ Clark: "The Determination of Hydrogen Ions." Second edition (1922).

² Ellis: J. Am. Chem. Soc., 38, 737 (1916).

³ Beans and Hammett: J. Am. Chem. Soc., 47, 1216 (1925).

⁴ Lewis, Brighton and Sebastian: J. Am. Chem. Soc., 39, 2245 (1917).

⁵ Tolman and Ferguson: J. Am. Chem. Soc., 34, 232 (1913).

Procedure

Throughout this work the usual potentiometric set-up was used with a Leeds and Northrup Type K potentiometer. A modification of the Hildebrand form of hydrogen electrode was used with a saturated potassium chloride calomel electrode. The hydrogen was generated by the electrolysis of sodium hydroxide solution. It was purified by being passed through alkaline permanganate solution, cotton, water and the same solution of which the hydrogen ion concentration was being determined. The solution was surrounded by a bath constant to $\pm 0.1^\circ$. The electrodes used consisted of pieces of platinum foil 15 mm. \times 5 mm. fused on to a piece of platinum wire and into a glass tube as recommended by Clark. Contact was made by filling the tube with mercury. All salts used were recrystallized and the mercury for the calomel electrode redistilled.

Use of the Bovie Titration Cell

When an open beaker was used for hydrogen ion determination, ten minutes were required for a thinly coated electrode to attain equilibrium. When a Bovie titration cell was substituted the time was reduced to three minutes. The latter has the advantage that the current of hydrogen stirs the solution and maintains an atmosphere of hydrogen above the solution. It is necessary to have the solution saturated with hydrogen before equilibrium can be obtained. Until then the electrode behaves more or less as an oxygen electrode.

Use of Gold Plated Electrodes

A preliminary plating of gold on the electrode is recommended by Lewis Brighton and Sebastian⁴ because gold, unlike platinum, does not absorb large amounts of gases and therefore comes to equilibrium more quickly. A comparison of electrodes plated with and without gold showed no difference when placed in a solution already saturated with hydrogen, both requiring three to five minutes to attain equilibrium. This is in accord with the results of Beans and Hammett who concluded that the massive platinum need not be saturated with hydrogen.

However, since a slightly more adherent coating of platinum black is obtained when the electrode is gold plated and since the deposit is more easily removed when electrolyzed in hydrochloric acid, gold plated electrodes were used throughout this work and are recommended.

Use of Lead Acetate in Platinizing Solution

Only a very slight deposit could be obtained on a platinum electrode when chemically pure chloroplatinic acid solution was used. This electrode gave a fluctuating reading, smaller than the proper value, when placed in a buffer solution. An unsuccessful attempt was made to obtain a deposit of platinum black from pure chloroplatinic acid solution using a 110 volt current. This only resulted in the formation of a sludge in the vessel. The minimum quantity of lead acetate required to produce a good deposit was found to be 0.5 cc. of a 0.1 N solution in 100 cc. of 3% chloroplatinic acid solution. Electrodes prepared in this way agreed to 0.1 millivolt.

Current Density in Plating

No noticeable difference could be obtained over a considerable range of current density but good results were obtained with a current of 20 milliamperes from two dry cells in series connected through a variable resistance. This current was maintained after the bubbles of gas were being evolved. As the electrodes had a surface of 1.5 sq. cm. this corresponds to a current density of about 1.35 amperes per square decimeter.

Nature of Deposit

Electrodes were prepared from solutions of chloroplatinic acid containing enough additional hydrochloric acid to make the total acidity 0.5 N and from solutions containing no additional acid. A comparison of the time required for equilibrium was made in a borax-boric acid buffer solution, a potassium chloride-hydrochloric acid buffer, a solution of borax and a solution of sulfuric acid. Both thinly and thickly plated electrodes were compared. The former were platinized in five minutes and the latter in forty-five.

TABLE I
Effect of Acidity on Plating the Electrodes

| | H_2PtCl_6 | | $H_2PtCl_6 + HCl$ | |
|-----------------|-------------|---------|-------------------|------------|
| | Thin | Thick | Thin | Thick |
| Borax | 3 min. | 7 min. | 4-7 min. | 20-25 min. |
| Alkaline buffer | 3 " | 15-20 " | 4-5 " | 10-12 " |
| Sulfuric acid | 5 " | 7-10 " | 3 " | 7-10 " |
| Acid buffer | 4 " | 10-12 " | 3-4 " | 7 " |

No great difference in time for equilibrium is caused by the acidity of the platinizing solution when the thinly plated electrode is used. The thick deposit from strongly acid solution requires more time in alkaline solutions than in acid. In all cases the thick deposit requires considerably more time for equilibrium. As the same reading is obtained with the thin deposit the latter is recommended. Another argument for the use of the thin deposit is found in the work with phthalate buffers. Merrill,¹ and Oakes and Salisbury² found a drifting in potential when used in a phthalate buffer. Clark³ and Wood and Murdick⁴ could find no such drift. Draves and Tartar⁵ showed that the reduction is due to the use of a thickly coated electrode as employed by the former while the thin deposit used by Clark causes no reduction. The well-known catalytic activity of finely divided platinum should be reduced to a minimum.

¹ Merrill: J. Am. Chem. Soc., 43, 2688 (1921).

² Oakes and Salisbury: J. Am. Chem. Soc., 44, 948 (1922).

³ Clark: J. Am. Chem. Soc., 44, 1072 (1922).

⁴ Wood and Murdick: J. Am. Chem. Soc., 44, 2008 (1922).

⁵ Draves and Tartar: J. Am. Chem. Soc., 47, 1226 (1925).

Directions for Plating Electrodes

The following method of plating platinum black electrodes is recommended, although other conditions may give equally good results:

1. Clean electrode by electrolyzing as anode in concentrated hydrochloric acid until old deposit is removed. New electrodes should be cleaned in hot alkali.

2. Electrolyze as cathode in a dilute potassium cyanide solution of gold. The directions of Clark for preparing this solution are:—Dissolve 0.7 g. gold chloride in 50 cc. water and precipitate the gold with ammonia water, taking care to avoid excess. Filter, wash and dissolve immediately in a KCN solution consisting of 1.5 g. KCN in 100 cc. water. Boil till the solution is free from the odor of ammonia.

3. Electrolyze as cathode for five minutes in a 3% solution of chloroplatinic acid containing 0.5 cc. of 0.1 N lead acetate in 100 cc. A current density of 1.35 amperes per square decimeter is employed.

4. Electrolyze as cathode in dilute sodium hydroxide solution a few seconds.

5. Electrolyze as cathode in dilute sulfuric acid one minute.

6. Keep in distilled water till ready for use.

No advantage was found in reversing the current during the deposition of platinum black.

Poisoning of Electrodes

The decrease in potential of the hydrogen-calomel electrode system after continued use is considered by Bovie and Hughes¹ as due to a poisoning by mercuric chloride. In the calomel electrode the following decomposition takes place:



Evidence of this is found in the gray color the calomel assumes and in a positive test for mercuric chloride in the potassium chloride solution. The mercuric chloride diffuses into the titrating chamber where it poisons the finely divided platinum.

If this is the cause, then, whether the poisoning is due to the mercuric chloride itself, a product of reduction, or a product of interaction with ma-

TABLE II
Removal of "Poisons" from Electrodes

| Poisoned by | Reading before poisoning Mv. | Reading after poisoning Mv. | Reading after treatment Mv. |
|--------------------------|---------------------------------|--------------------------------|--------------------------------|
| Hg Cl ₂ soln. | 592.1 | -200 | 592.2 |
| " " | 592.1 | -44 | 592.3 |
| " " | 593.2 | -238 | 593.1 |
| " " | 587.8 | -302 | 587.6 |
| Electrode soln. | 590.5 | -200 | 590.5 |
| " " | 587.6 | -200 | 587.5 |

¹ Bovie and Hughes: J. Am. Chem. Soc., 45, 1904 (1923).

materials in the solution, it should be removed, in most cases at least, by nitric acid. It was observed by one of us that the potential could be restored at least qualitatively by such treatment. Table II shows the results of a quantitative study of the poisoning by mercuric chloride solution and the solutions from calomel electrodes and the removal of the poison.

In all cases after treatment with nitric acid, the electrode was electrolyzed a few seconds in sodium hydroxide solution and then in sulfuric acid. This removes the nitric acid and saturates the electrode with hydrogen. The poisoning was much more readily effected when a thickly coated electrode was used, another argument for a thin deposit. Extreme difficulty was found in poisoning electrodes. Apparently, when repurified chemicals are used throughout, the poisoning danger is not as great as with ordinary chemicals. Attempts to poison the electrode with formaldehyde, phenol, and potassium cyanide were unsuccessful. An electrode poisoned with the solution from a calomel electrode was also restored by treatment with dichromate cleaning mixture.

Summary and Conclusions

1. The hydrogen electrode attains equilibrium more quickly in a Bovie titration cell than in an open beaker.
2. A preliminary plating of gold on electrodes does not effect the time required for attainment of equilibrium but causes a more adherent coating of platinum black to be deposited which is more easily removed in cleaning.
3. A thinly coated electrode is more desirable than a heavily coated one.
4. Directions for plating electrodes are given.
5. Poisoning due to mercuric chloride can be removed by treatment with nitric acid or dichromate cleaning mixture.

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ADSORPTION BY CADMIUM SULFIDE AND ITS IMPORTANCE IN THE ESTIMATION OF CADMIUM

BY HARRY B. WEISER AND EDWARD J. DURHAM

Precipitated cadmium sulfide is always contaminated by anions in the solution from which it separates. The determination of cadmium as sulfide, especially in the presence of sufficient hydrochloric acid to ensure its separation from zinc, has long been regarded as a useless method because of the chloride carried down with the precipitate. Treadwell¹ attributes the contamination to the formation of a double salt, $\text{CdS} \cdot \text{CdCl}_2$, in varying amounts depending on the acid concentration and the temperature and pressure at which the precipitation is carried out. Egerton and Raleigh² believe the precipitate to have a constant composition when thrown down at 80° from a solution containing four cubic centimeters of concentrated hydrochloric acid in 100 cubic centimeters, and washed with an unspecified, definite quantity of water. Under these conditions, the precipitate is said to contain 3.57 percent of chlorine as the alleged salt, $\text{CdS} \cdot \text{CdCl}_2$; hence, in determining cadmium quantitatively by weighing the sulfide, the molecular weight of the precipitate is taken to be 147.4 instead of 144.47 for pure cadmium sulfide.

Since conclusive evidence of the existence of a definite double salt $\text{CdS} \cdot \text{CdCl}_2$ is lacking, it is probable that the contamination of the sulfide gel is due to adsorption of cadmium chloride in varying amounts depending on

TABLE I
Adsorption of Chloride by Cadmium Sulfide precipitated at 25° .
(Fig. 1, Curve A)

| Cubic centimeters of N/10 CdCl_2 Total volume 75 cubic centimeters | Final normality of HCl | Chlorine adsorbed Grams | $\frac{\text{Cl}}{\text{Cds}^*} \times 100$ |
|--------------------------------------------------------------------------------------|---------------------------|----------------------------|---------------------------------------------|
| 25 | 0.033 | 0.00361 | 2.00 |
| 25 | 0.068 | 0.00467 | 2.59 |
| 25 | 0.121 | 0.00644 | 3.51 |
| 25 | 0.156 | 0.00764 | 4.23 |
| 25 | 0.209 | 0.00815 | 4.51 |
| 25 | 0.349 | 0.00947 | 5.24 |
| 25 | 0.419 | 0.00996 | 5.52 |
| 25 | 0.407 | 0.00945 | 5.23 |
| 25 | 0.596 | 0.00923 | 5.11 |
| 25 | 0.664 | 0.00674 | 3.73 |

* Corresponding to 25 cc. of N/10 CdCl_2 .

¹ Treadwell-Hall: "Analytical Chemistry," 2, 190 (1924).

² J. Chem. Soc., 123, 3019 (1923).

conditions. To test this hypothesis, hydrogen sulfide at room temperature was passed into a definite volume of solution containing a constant amount of cadmium chloride and varying amounts of hydrochloric acid. The precipitate was filtered on a Gooch crucible, washed until the wash water gave no test for chloride and then analyzed for the chloride content. This was accomplished by dissolving the precipitate in nitric acid, adding an approximately constant excess of silver nitrate, filtering through a Gooch crucible and titrating the excess silver nitrate with ammonium thiocyanate according to Volhard's method. The results are given in Table I and shown graphically by curve A, Fig. 1. The filtrates were tested for completeness of precipitation

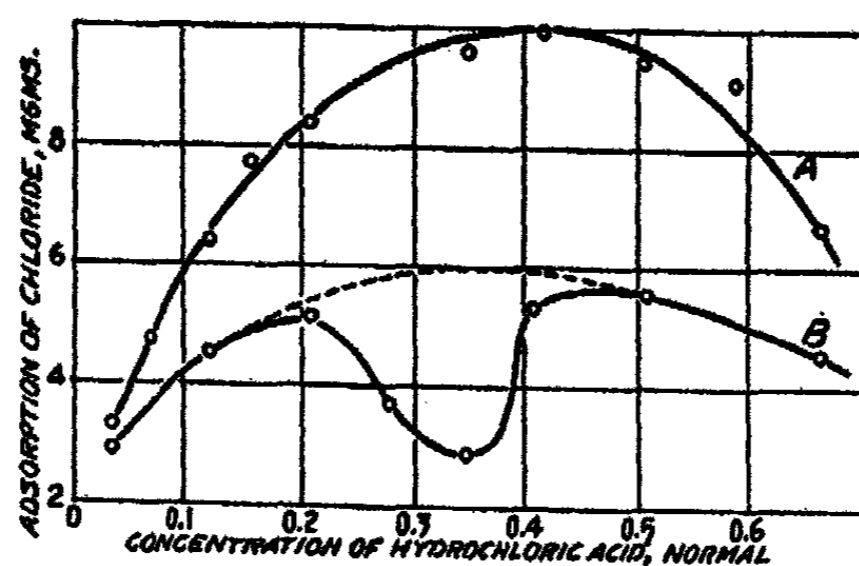


FIG. 1

by rendering them alkaline with ammonia and saturating with hydrogen sulfide. With the most acid solution a faint yellow coloration was noted but no precipitate. The amount of cadmium required to produce this coloration was found to be negligible as compared with the total amount of precipitate.

An attempt was made to repeat the above observations at 80° as recommended by Egerton and Raleigh, but precipitation was found to be far from complete. Accordingly, the several solutions were heated at 80° , removed from the source of heat, and hydrogen sulfide conducted through continuously while they cooled down to room temperature. The precipitates were washed and analyzed for chloride with the results given in Table II and shown graphically in curve B of Fig. 1.

Referring to curve A, it will be seen that the amount of chlorine in the precipitate does not increase continuously with the concentration of hydrochloric acid but exhibits a maximum. This maximum is due to a visible change in the physical character of the precipitate from a flocculent to a distinctly granular structure. The curve is thus a typical adsorption curve showing a maximum due to a physical change in the adsorbent.¹

Curve B for the second series of the experiments lies under curve A as would be expected since the temperature at which the precipitation starts is

¹ Cf. Lottermoser and Rothe: *Z. physik. Chem.*, 62, 359 (1908); Weiser: "The Hydrous Oxides," 330-332 (1926).

TABLE II

Adsorption of Chloride by Cadmium Sulfide precipitated between 80° and 25°.
(Fig. 1, Curve B)

| Cubic centimeters of N/10 CdCl ₂ Total volume 75 cubic centimeters | Final normality of HCl | Chlorine adsorbed Grams | $\frac{\text{Cl}}{\text{CdS}} \times 100$ |
|----------------------------------------------------------------------------------------|---------------------------|----------------------------|-------------------------------------------|
| 25 | 0.033 | 0.00288 | 1.59 |
| 25 | 0.121 | 0.00452 | 2.50 |
| 25 | 0.209 | 0.00506 | 2.80 |
| 25 | 0.279 | 0.00364 | 2.02 |
| 25 | 0.349 | 0.00287 | 1.59 |
| 25 | 0.419 | 0.00538 | 2.98 |
| 25 | 0.507 | 0.00558 | 3.09 |
| 25 | 0.664 | 0.00459 | 2.54 |

* Corresponding to 25 cc. of N/10 CdCl₂.

higher, hence the precipitate is more granular and the adsorption less. With increasing concentration of acid, the adsorption of chloride increases to a maximum so that the first part of curve B is very similar to that of curve A, and for the same reason. But when the acid reaches a concentration in the neighborhood of 0.3 normal, the amount of cadmium sulfide precipitated in the hot decreases with a corresponding increase in the amount precipitated at lower temperatures. This means a larger amount of more finely divided particles and a correspondingly greater adsorption which rises to a second maximum as the concentration of acid is further increased. This behavior would be difficult to explain on the basis of double salt formation but is readily accounted for by considering the contamination as a case of adsorption. The dotted curve would probably represent the adsorption if the amount of salt precipitated at each temperature during cooling were constant. The final concentration of acid recommended by Egerton and Raleigh was approximately 0.5 normal. This might appear to account for the constancy of composition of their precipitates since curve B is relatively flat when the hydrochloric acid concentration is in the neighborhood of 0.5 normal. However, the chlorine content under these conditions corresponds to 12.2 percent of the alleged double salt instead of to 16.5 percent as calculated from Egerton and Raleigh's results.¹ The difference is, of course, in the conditions of the precipitation. Although the above authors do not say, it is probable that they carried out the precipitation as far as possible at 80° and completed the process at room temperature. If so, they should have obtained a greater proportion of relatively larger particles and a correspondingly smaller adsorption than was obtained by the procedure employed by us. The larger

¹ Egerton and Raleigh claim that 3.57 percent of chlorine in say 0.1435 gram of the cadmium sulfide precipitate corresponds to 8.16 percent of the alleged double salt, but this appears to be incorrect. 3.57 percent of 0.1435 gram is 0.00512 gram of chlorine which is equivalent to 0.0238 grams of the alleged CdS·CdCl₂. This amount is 16.6 percent of 0.1435 gram, the total weight of the precipitate.

percentage of chlorine in their precipitates may have resulted from incomplete washing, from the presence of ammonium chloride together with hydrochloric acid in the solution from which the sulfide separated, or from both. In any event, the procedure outlined by Egerton and Raleigh is not sufficiently definite to be of value under the varying conditions which are encountered in technical practice.

Summary

The results of this investigation may be summarized as follows:

1. Cadmium sulfide thrown down from hydrochloric acid solution carries down chloride in varying amounts depending on the acid concentration, the temperature, and the pressure at which the precipitation is carried out. The contamination is due to adsorption and not to the formation of a definite double salt, $\text{CdS} \cdot \text{CdCl}_2$.
2. Determinations were made of the adsorption of chloride by cadmium sulfide precipitated from solutions containing varying amounts of hydrochloric acid, (A) at a temperature of 25° ; and (B) by conducting H_2S continuously into the solutions while they cool from 80° to 25° . The precipitation of cadmium sulfide is incomplete at 80° .
3. Continuous curves are obtained by plotting the amount of chloride adsorbed by a definite weight of cadmium sulfide against the hydrochloric acid concentration of the solution. Curve A (25°) is a typical adsorption curve with a maximum due to a physical change in the adsorbent from a flocculent to a distinctly granular structure as the acid concentration is increased. Curve B (80° - 25°) lies below that obtained at 25° since the precipitate formed at the higher temperature is more granular and the adsorption correspondingly less. The first part of the curve is similar to curve A and for the same reason: but when the acid concentration is in the neighborhood of 0.3 normal, the amount of salt precipitated in the hot decreases with a corresponding increase in the amount precipitated at lower temperatures. This gives a larger amount of more finely divided particles and a correspondingly greater adsorption which rises to a second broad maximum as the concentration of the acid is further increased.
4. The determination of cadmium as sulfide under technical conditions is of doubtful value since it is questionable whether the conditions of precipitation can be maintained sufficiently constant to obtain a cadmium sulfide precipitate with a constant amount of adsorbed chloride.

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STUDIES IN HOMOGENEOUS GAS REACTIONS II* INTRODUCTION OF QUANTUM THEORY

BY LOUIS STEVENSON KASSEL**

Introduction

In a preceding paper of this series the author¹ has presented the elements of a theory of unimolecular reactions. In this theory it is assumed that activation is by collision, that the molecules have many internal degrees of freedom, and that reaction occurs when some special degree of freedom acquires at least a critical amount of energy; as has been frequently pointed out recently, all the substances known to decompose unimolecularly in the gaseous state have complex molecules. In the former paper it was assumed that all the degrees of freedom are classical. This is of course not a very accurate representation of an actual molecule. The same theory will now be applied to a hypothetical molecule consisting of a number of quantum oscillators, all of the same frequency, or of frequencies which are commensurable. If the molecule contains oscillators of different frequencies, which are incommensurable, it is not possible for energy to be transferred directly from one to the other. Of course, if there are any classical oscillators in the molecule, they could act as a "bridge" over which the energy could pass; in the absence of classical oscillators, there would be some parts of the molecule which could contribute no energy to the critical oscillator, and these parts would have no effect on the reaction.

Just how this is to be interpreted physically is not certain. It seems likely that an oscillator will either have no effect at all, or else an effect very nearly the same as if it were of a commensurable frequency not too greatly different from its own. In either case, a sufficiently good representation could be obtained by a model in which all the frequencies were commensurable.

Mathematical Part

Suppose that there are s oscillators in the molecule, all of frequency ν such that

$$m h \nu = \epsilon_0$$

where ϵ_0 is the critical energy, that is, the amount of energy which must accumulate in the critical oscillator in order for reaction to occur.

Since we are dealing with a quantum case, all the integrals which arose in the classical theory are replaced by summations. Thus the general formulae given by Rice and Ramsperger² assume the forms

* Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 169.

** National Research Fellow in Chemistry.

¹ Kassel: *J. Phys. Chem.*, 32, 225 (1928).

² Rice and Ramsperger: *J. Am. Chem. Soc.*, 49, 1617 (1927).

$$K = \sum_{n=m}^{\infty} \frac{W_n b_n}{1 + \frac{b_n k T}{a p}} \quad (1)$$

and

$$K_{\infty} = \sum_{n=m}^{\infty} W_n b_n \quad (2)$$

Here W_n is the fraction of all the molecules which would have exactly n quanta at equilibrium, if no reaction occurred, b_n is the specific reaction rate of these molecules, and

$$a = 4 \sigma^2 \sqrt{\frac{\pi k T}{m}}$$

It is easily shown that

$$W_n = \alpha^n (1 - \alpha)^s \frac{(n + s - 1)!}{n! (s - 1)!} \quad (3)$$

where

$$\alpha = e^{-h\nu/kT}$$

and s is the number of degrees of freedom.¹

We make the same assumption for the evaluation of b_n that was made for b_0 in the classical case, namely, that it is proportional to the fraction of all the molecules of the kind and energy content in question, which would have at least the critical energy in the critical oscillator if no reaction occurred, and equilibrium were reached. The author² has shown that this fraction is

$$\frac{n! (n - m + s - 1)!}{(n - m)! (n + s - 1)!} \quad (4)$$

Substitution of these values of W_n and b_n in (2) gives the result

$$\begin{aligned} K_{\infty} &= \sum_{n=m}^{\infty} A \alpha^n (1 - \alpha)^s \frac{(n - m + s - 1)!}{(n - m)! (s - 1)!} \\ &= A \alpha^m (1 - \alpha)^s \sum_{p=0}^{\infty} \alpha^p \frac{(p + s - 1)!}{p! (s - 1)!} \end{aligned}$$

where we have substituted $m + p$ for n . But

$$\frac{(p + s - 1)!}{p! (s - 1)!}$$

is just the coefficient of α^p in the expansion of $(1 - \alpha)^{-s}$.

Hence

$$\sum_{p=0}^{\infty} \alpha^p \frac{(p + s - 1)!}{p! (s - 1)!} = (1 - \alpha)^{-s},$$

and

$$K_{\infty} = A \alpha^m = A e^{-mh\nu/kT} = A e^{-\epsilon_0/kT} \quad (5)$$

¹ As the term is used here, and from now on, the number of degrees of freedom is equal to the number of oscillators. This differs from the usage of the former paper, where the number was taken as the number of squared terms in the energy function.

² Kassel: Proc. Nat. Acad. Sci., 14, 23 (1928).

This is formally identical with the result obtained when classical oscillators were used; the interpretation of the constant A is exactly the same as before.

Substitution of these same values in (1) gives, upon simplification, the result

$$K/K_{\infty} = (1 - \alpha)^s \sum_{p=0}^{\infty} \frac{\alpha^p \frac{(p + s - 1)!}{p! (s - 1)!}}{1 + \frac{A}{aN} \frac{(p + m)! (p + s - 1)!}{(p + m + s - 1)! p!}} \quad (6)$$

where N is the number of molecules per cubic centimeter.

Now consider the case of two different frequencies. Suppose that there are s oscillators of frequency ν and r of frequency μ , where

$$\mu = t\nu,$$

t being an integer. Let the critical energy be $m h \nu$, and suppose that the critical oscillator is of the frequency ν . (This is the case which seems of most interest physically, since we may picture the reaction as occurring at a "bond" which is not very strong, and hence one which is associated with a low frequency.) It is easy to show, by the same methods as were used for the preceding case that

$$W_n = (1 - \alpha)^s (1 - \alpha^t)^r \alpha^n \sum_{v=0}^k \frac{(n - tv + s - 1)! (v + r - 1)!}{(n - tv)! (s - 1)! v! (r - 1)!},$$

$$\text{and } b_n = A \frac{\sum_{v=0}^1 \frac{(n - m - tv + s - 1)! (v + r - 1)!}{(n - m - tv)! (s - 1)! v! (r - 1)!}}{\sum_{v=0}^k \frac{(n - tv + s - 1)! (v + r - 1)!}{(n - tv)! (s - 1)! v! (r - 1)!}},$$

where $n/t - 1 < k \leq n/t$, and $(n - m)/t - 1 < 1 \leq (n - m)/t$.

Hence

$$K_{\infty} = A \alpha^m (1 - \alpha)^s (1 - \alpha^t)^r \sum_{p=0}^{\infty} \sum_{v=0}^1 \alpha^p \frac{(p - tv + s - 1)! (v + r - 1)!}{(p - tv)! (s - 1)! v! (r - 1)!}$$

The double summation, however, is evidently the expansion of

$$(1 - \alpha)^{-s} (1 - \alpha^t)^{-r}$$

and hence this reduces to the same simple expression as before,

$$K_{\infty} = A e^{-mh\nu/kT} = A e^{-\epsilon_0/kT}.$$

It is useless to write down the rather complex expression which is found for K . In practice, numerical values of $W_n b_n$ and of b_n are calculated for the chosen values of s , r , t , m , and T , for all values of n such that the contribution to the sum is appreciable. These values are substituted directly into (1). In making the computations, the values for the logarithms of the binomial coefficients were taken from Glover's table¹.

¹ Glover: "Tables of Applied Mathematics in Finance, Insurance, Statistics," 459 (1923).

These formulae may be extended without difficulty to the case where t is rational but not integral, and to the case of more than two frequencies. The amount of computation that would be necessary in the use of the more general formulae, as well as the fact that the results which are obtained when two different frequencies are used are much the same as for a single frequency, makes it useless at the present time to consider more than two frequencies. If we were able to obtain complete information from some other source, say from spectral data and specific heat values, as to the frequencies of all the oscillators in a substance which has been found to decompose unimolecularly, it might be worth while to see how nearly the experimental values for its reaction rates could be reproduced by a model which has just those frequencies. Such information does not exist at present.

Application to Nitrogen Pentoxide

It requires six coordinates to fix the position and orientation of a rigid body; the seven atoms in nitrogen pentoxide have 21 coordinates, so that there must be fifteen coordinates which correspond to internal degrees of freedom. That is, $s = 15$. Even if all of these degrees of freedom were classical, it would not be easy to account for the maintenance of the rate in this reaction. We have

$$E_0 = 24700 \text{ calories,}$$

$$A = 4.56 \times 10^{-13},$$

and if we take

$$T = 300^\circ,$$

$$s = 15,$$

$$\sigma = 10^{-7} \text{ cm.,}$$

and use the formula given in the preceding paper, we find the results given in Table I.

TABLE I

| Pressure cm | K/K _∞ | Pressure cm. | K/K _∞ |
|----------------|------------------|-----------------|------------------|
| 3.1 | .9968 | .031 | .8797 |
| .31 | .9751 | .0031 | .6580 |

The recent work of Hibben¹ seems to require better maintenance of the rate than this at a pressure of .003 cm.; it might be possible, however, by increasing somewhat the value assumed for the diameter and by postulating a reaction chain two molecules long, to account for Hibben's results. But it is surely not allowable to assume that the fifteen degrees of freedom are all classical. Equation (6) has been used to calculate values of K/K_∞ for the quantum case, with various values assigned for the frequency; the results are presented in Table II.

¹ Hibben: Proc. Nat. Acad. Sci., 13, 626 (1927); J. Am. Chem. Soc., 50, 940 (1928).

TABLE II
Values of K/K_{∞}

| Pressure cm. | $m = \infty$ $\lambda = \infty$ | $m = 27$ $\lambda = 31.11\mu$ | $m = 18$ $\lambda = 20.74\mu$ | $m = 9$ $\lambda = 10.37\mu$ |
|-------------------------|------------------------------------|----------------------------------|----------------------------------|---------------------------------|
| 31. | — | .9995 | .999 | .990 |
| 3.1 | .997 | .995 | .991 | .920 |
| .31 | .975 | .962 | .939 | .598 |
| .031 | .880 | .831 | .752 | .143 |
| .0031 | .658 | .561 | .429 | — |
| Mol. heat (cal/deg) | 29.80 | 24.58 | 19.51 | 6.45 |
| Heat con- tent (cal) | 8941 | 3769 | 2287 | 416 |

In the last lines of this table the contributions of these oscillators to the molecular heat and to the heat content, at 300°K., are given; the contributions due to translation and rotation must be added to these figures, to get the usual values.

The specific heat of nitrogen pentoxide has never been measured; it is reasonable to suppose that the vibrational heat content is about 3000 calories at 300°K.; this would mean a total heat content of about 4800 calories, which is not unreasonably large. This would be given by assigning a frequency corresponding to about 25μ to each of these oscillators. There are certainly some frequencies in the molecule which are higher than this, since Warburg and Leithäuser¹ found absorption bands at 3.39μ and at 5.81μ . If there were not too many oscillators of these frequencies, their presence could be compensated by other oscillators of very low frequencies.

Thus, on the basis of a rough estimate of the heat content, it is possible to account for about 50% maintenance of the reaction rate at the lowest pressures studied, and practically complete maintenance at pressures about a hundred-fold higher. If this discrepancy is to be accounted for simply by increasing the rate of production of activated molecules by collision, it would be necessary to increase this rate a hundred-fold, which could be done by increasing the diameters for collisional deactivation tenfold, to 10^{-8} cm. Bernard Lewis² has attempted to justify such values; it seems to the author, however, that while it is undoubtedly permissible to use values somewhat in excess of kinetic theory values, it is not reasonable to expect deactivational diameters as large as those found for metal atoms which are electronically excited; the reasons for this are two-fold: first, the resonance between single atoms is undoubtedly more perfect than between molecules, since in the latter all the frequencies are to some extent mutually dependent, a change in the rotational state altering slightly the vibrational frequencies; and

¹ Warburg and Leithäuser: *Ann. Physik*, 28, 313 (1909).

² B. Lewis: *Science*, 66, 331 (1927).

second, for the de-excitation of an atom of mercury or cadmium in the experiments quoted by Lewis, only a single quantum must be removed, while for the de-activation of an activated molecule several quanta may have to be lost. In fact, in all the cases of importance in maintaining the rate, de-activation involves the loss of more than a single quantum, since it is the activated states of highest energy which are depleted first and most when the rate begins to fall off, and hence it is only the rate of production of these states which needs to be increased to maintain the rate.

This last fact suggests that perhaps the action of radiation is of importance at low pressures. Indeed, it seems likely that the action of the thermal radiation alone tends to maintain the Maxwell-Boltzmann distribution; the requirement for this tendency is that for each activated state the rate at which molecules leave this state through radiation (spontaneous or induced) is equal to the rate at which molecules enter the state through absorption of radiation, when equilibrium is reached. Thus the rate of production of activated molecules through collision is augmented by the rate of production by absorption of radiation, and it is probable that this effect is relatively greatest for the molecules of greatest energy content. It is not clear just how the absolute magnitude of this effect can be calculated. If it exists it should be possible to obtain a photochemical decomposition of nitrogen pentoxide with infra-red light at very low pressures, where the deactivating influence of collisions is greatly reduced. Of course, the active radiation may lie in the extreme infra-red.

At least, the difficulty in accounting for the experimentally observed reaction rate is not so insurmountable as it has formerly seemed. It cannot be decided at present whether the explanation will be found in larger diameters, or in a combination of activation by collisions and by radiation, the former being effective at higher pressures, the latter at lower, or in some sort of "coupling" between molecules as has been suggested by Polanyi¹ or in the abandonment of the First Law except as a statistical principle, as has been suggested by Tolman² and definitely proposed by J. J. Thomson³. At the present time, any of these explanations is sufficiently plausible to merit further consideration.

Application to Azomethane

Since azomethane has ten atoms, there must be 24 internal degrees of freedom. This number is much greater than was found necessary for the interpretation of the experimental results with classical degrees of freedom. In fact, the data of Ramsperger⁴ on the decrease of reaction rate with pressure can be very well reproduced by assuming $s = 12$, as the writer showed in the preceding paper.

¹ Polanyi: *Z. Physik*, 1, 337; 2, 90; 3, 31 (1920).

² Tolman: *J. Am. Chem. Soc.*, 47, 1552 (1925).

³ Thomson: *Phil. Mag.*, 3, 241 (1927).

⁴ Ramsperger: *J. Am. Chem. Soc.*, 49, 1495 (1927).

Calculations have been made, using equation (6), taking $s = 24$, $\sigma^2 = 1.5 \times 10^{-14}$, for temperatures of 563.1°K . and 603.1°K ., the two temperatures at which Ramsperger measured the decrease in rate, and for a number of frequencies. The results of these calculations are given in Tables III and IV. For purposes of comparison, the theoretical values with classical degrees of freedom, taking $s = 12$ and $s = 9$, are included in these tables. The values for $s = 12$ are not exactly the same as those given in the preceding paper, slightly different values for A and E_0 having been used in the calculations; the agreement with experiment is very slightly better than that of the earlier values. The values of A and E_0 which are used here have been obtained from a consideration of those experiments which were made at the highest pressures; they are

$$A = 3.135 \times 10^{16},$$

$$E_0 = 52441 \text{ calories.}$$

TABLE III
Azomethane 603.1°K .
Values of K/K_∞

| Press cm. | $s = 24$ $m = 32$ $\lambda = 17.37\mu$ | $s = 24$ $m = 25$ $\lambda = 13.57\mu$ | $s = 24$ $m = 15$ $\lambda = 8.142\mu$ | $s = 24$ $m = 10$ $\lambda = 5.428\mu$ | $s = 12$ classical | $s = 9$ classical |
|------------|----------------------------------------------|----------------------------------------------|----------------------------------------------|----------------------------------------------|-----------------------|----------------------|
| 620 | — | — | — | — | — | .860 |
| 62 | — | .998 | .994 | .963 | .874 | .591 |
| 6.2 | .985 | .986 | .952 | .795 | .640 | .279 |
| .62 | .940 | .924 | .812 | .379 | .348 | .0931 |
| .062 | .789 | .750 | .518 | .0651 | .140 | — |
| .0062 | .535 | .479 | .214 | .00703 | .0426 | — |
| .00062 | .280 | .228 | .0413 | .000709 | — | — |
| mol. heat | 40.91 | 37.13 | 24.53 | 11.78 | 23.84 | 17.88 |
| heat cont. | 13444 | 10553 | 4796 | 1602 | 14379 | 10785 |

TABLE IV
Azomethane 563.1°K .
Values of K/K_∞

| Press cm. | $s = 24$ $m = 15$ $\lambda = 8.142\mu$ | $s = 24$ $m = 10$ $\lambda = 5.428\mu$ | $s = 12$ classical | $s = 9$ classical |
|-----------|----------------------------------------------|----------------------------------------------|-----------------------|----------------------|
| 560 | — | — | — | .891 |
| 56 | .997 | .970 | .910 | .648 |
| 5.6 | .972 | .819 | .707 | .337 |
| .56 | .857 | .396 | .417 | .123 |
| .056 | .584 | .0677 | .182 | — |
| .0056 | .257 | .00729 | .0596 | — |
| .00056 | .0501 | .000735 | — | — |

The last lines in Table III give the contribution of the internal energy to the molecular heat and to the heat content. On the basis of the molecular heat, we must reject the values for $m = 32$ and $m = 25$. The molecular heat for $m = 15$ is not unreasonably large, and the heat content is quite possibly too low. It is of interest to compare classical and quantum cases in which the molecular heat or the heat content is about the same. Thus the heat content for 9 classical oscillators (at 603.1°K .) is about the same as for 24 quantum oscillators, with $m = 25$; yet with the latter model the maintenance of the rate is tremendously better than with the former; also, the molecular heat for 12 classical oscillators is nearly the same as for 24 quantum oscillators with $m = 15$; here again the quantum model gives a much better maintenance of the rate, although the difference is not as great as in the preceding case.

In these comparisons, we have been using a fixed value for σ^2 , namely 1.5×10^{-16} . Of course, in applying the theoretical values to experimental data, we are at liberty to modify the value assumed for σ^2 ; the values of K/K_∞ are dependent upon p and σ^2 only through the term $p\sigma^2$ and hence when σ^2 is multiplied by any factor, p must be multiplied by the reciprocal of this factor. It is usually possible in this way to bring the theoretical values into agreement with experiment at a single temperature.

It is convenient to plot $\log K$ against $\log p$. This has been done for the data of Table III in Fig. 1, and for that of Table IV in Fig. 2. The experimental values are not included in these figures, but the curves for 12 classical degrees of freedom are in good agreement with the experimental curves. In these figures a change in the value assumed for σ^2 moves the entire curve in a direction parallel to the $\log p$ axis. It is evident from Fig. 1 that the quantum curves for $m = 32$, $m = 25$, and $m = 15$ can be brought into an approximate coincidence with the classical curve for $s = 12$ by a parallel displacement of this sort. The curve for $m = 10$ falls off much more sharply, and cannot be made to coincide with the classical curve. Hence, it is possible to fit the data at 603.1°K . by taking $s = 24$, m between 15 and 32, and assigning an appropriate value to σ^2 . It has already been seen that the molecular heat of the models with $m = 32$ and $m = 25$ is too large, and it is now found that for these models it would be necessary to assume a value of σ^2 of about $.5 \times 10^{-16}$ to bring the theoretical curve into agreement with experiment. The kinetic theory value is at least 40 times this large, so that the activated molecules would survive many collisions; but the present form of the theory is based upon the assumption that every collision is fatal to an activated molecule. The same equations would hold if an activated molecule had a definite chance of surviving a collision, this chance being independent of the energy of the activated molecule, and the energy of the other molecule, that is, of the temperature. If this were true, then we could interpret σ^2 as a target area, in the sense in which Fowler and Rideal¹ have used the term, rather than as a (diameter)². But it seems unlikely that this target area

¹ Fowler and Rideal: Proc. Roy. Soc., 113 A, 570 (1926).

should be independent of the energies involved, unless it is at least equal to the cross-section of a molecule.

Thus the models in which we have taken $m = 32$ and $m = 25$ are unsatisfactory, because their specific heats are too large and their cross-sections (or target areas) are too small. The curve for $m = 15$ can be brought into approximate agreement with experiment at this temperature by taking σ^2 equal to about 6×10^{-16} , which is still somewhat smaller than the probable kinetic theory value.

When the same value of σ^2 is used at the lower temperature, the agreement with experiment is very bad. In order to obtain approximate agreement

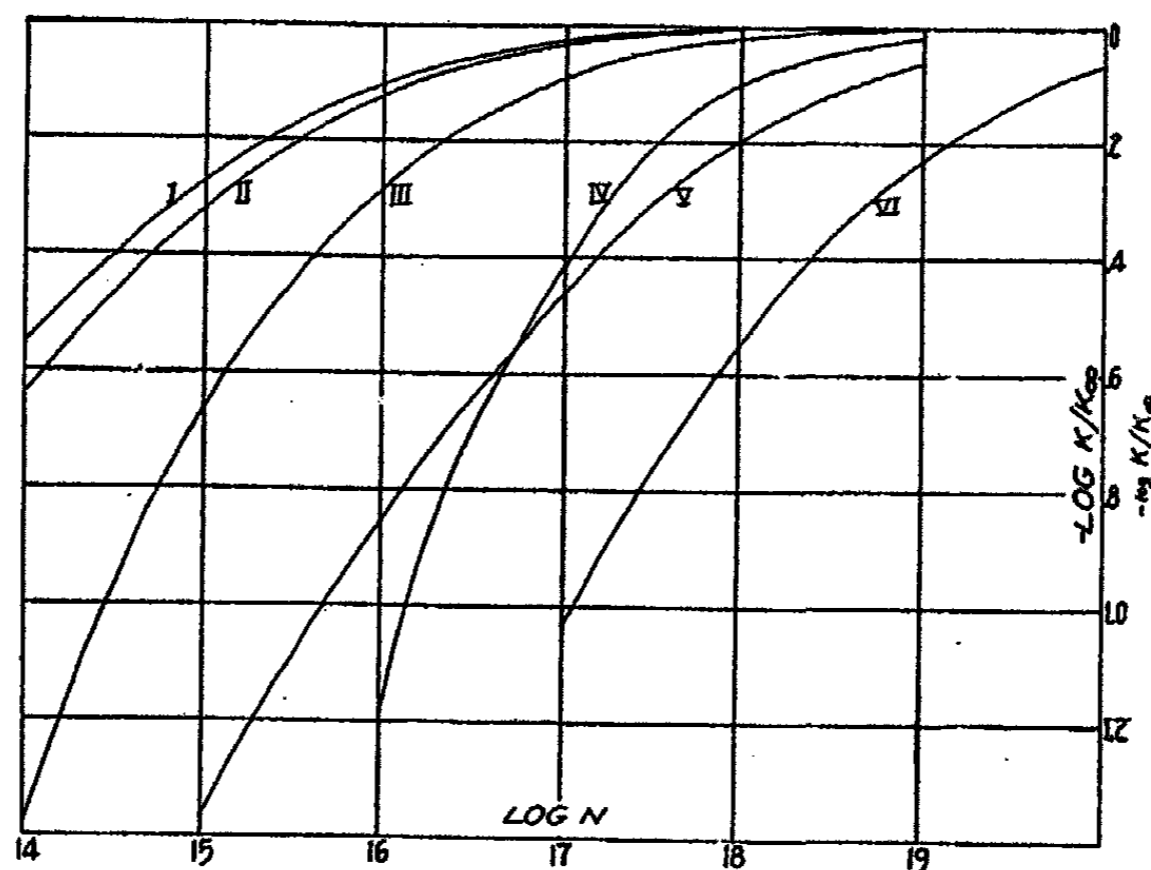


FIG. 1
603.1°K

I $s = 24, m = 32$
II $s = 24, m = 25$
III $s = 24, m = 15$

IV $s = 24, m = 10$
V $s = 12, \text{classical}$
VI $s = 9, \text{classical}$

with experiment at the two temperatures together, we take $\sigma^2 = 9.3 \times 10^{-16}$. The resulting curves are compared with the experimental data in Fig. 3. The agreement is not very satisfactory. The spread between the two theoretical curves is very much less than between the experimental points.

It is of interest to study the energies of the reacting molecules in the various models we have constructed. In Fig. 4 the contribution of the various quantum states to K_∞ is represented, for $T = 603.1^\circ$, $s = 24$, and $m = 40, 32, 25, 15$, and 10 . The total area of the different diagrams has been made the same, and the area of each rectangle is proportional to the fraction of K_∞ due to molecules in the corresponding quantum state. The diagrams for $m = 40$ and $m = 32$ have a striking resemblance to the curves in Fig. 1 of Rice and Ramsperger's article (*loc. cit.*); the frequencies here are low enough for the behavior of the system to be essentially classical. But the plot for

$m = 25$ has begun to deviate from the type of curve always obtained in the classical theory, that for $m = 15$ shows a much later stage in the change, and for $m = 10$ the change is almost complete; here the greater part of the reacting molecules come from a single quantum state, and hence have a single specific reaction rate. Thus when the frequency of the oscillators is made high enough, this theory reduces to something very like Theory I of Rice and Ramsperger; it differs from this theory only in the use of a quantum formula for the equilibrium concentration of activated molecules. It is

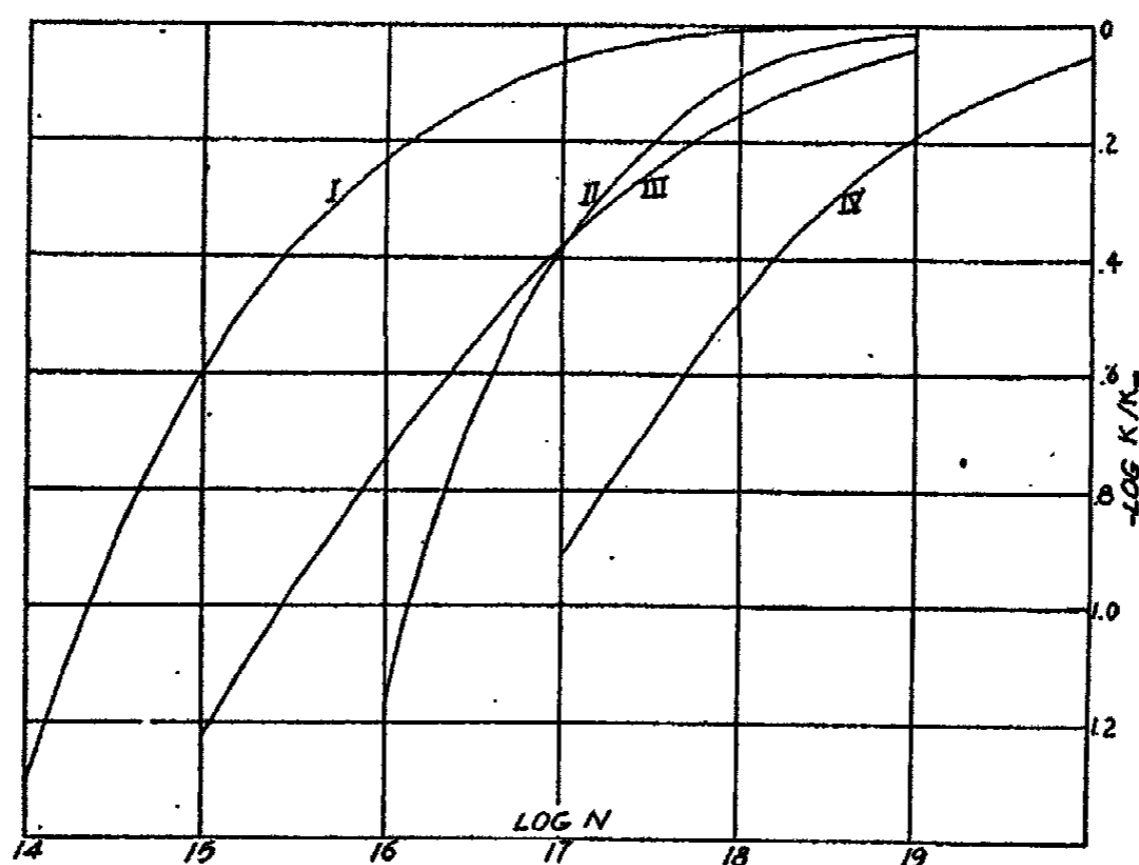


FIG. 2
563.1°K

I $s = 24, m = 15$
II $s = 24, m = 10$

III $s = 12, \text{classical}$
IV $s = 9, \text{classical}$

evident from equation (6) that when only the first term in the summation is important, which occurs when the frequencies are high enough, we may write

$$1/K = C + C'/p,$$

and hence that a plot of $1/K$ against $1/p$ will give a straight line. Therefore the curves for $\log K$ against $\log p$ will be of the same shape for high enough frequencies, regardless of the values which T , s , or m may have. In the preceding paper of this series, the writer has shown that, at least for most of the cases in which the rate has been found to fall off, the curves are not of this shape.

It is scarcely possible to say just what value of m is most satisfactory for azomethane, in conjunction with $s = 24$. The choice $m = 15$, gives a molecular heat which is about right, perhaps a little too high, a heat content which is quite possibly too low, a value of σ^2 which is about as small as it is safe to use, if it is assumed that collision always destroys an activated molecule, and

leads to curves at the two temperatures which do not spread apart sufficiently to give a really good agreement with experiment. It has been found, from a study of the numerous calculations which have been made on the basis of this theory, that the spread between the curves at two fixed temperatures, measured always at the same value of K/K_{∞} , increases as s increases and as the frequency of the oscillators decreases. Thus, in order to increase the spread in the present instance, keeping s constant, we would have to decrease the frequency, which would mean an increase in m . But this increase in m would increase the molecular heat, and decrease the value of σ^2 , and we have decided that neither of these changes is permissible. The agreement with experiment shown in Fig. 3 is therefore as good as can be obtained on

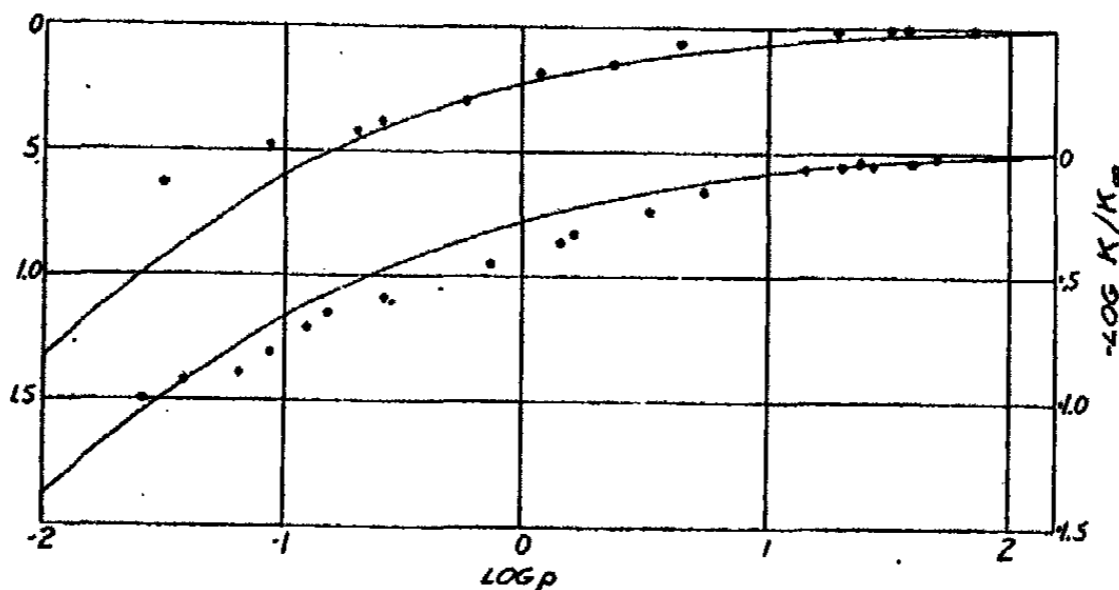


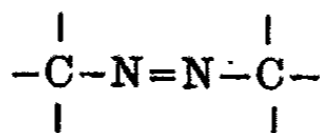
FIG. 3

Azomethane, $s = 24$, $m = 15$
 The ordinates to the right are for the lower curve,
 $T = 603.1^{\circ}\text{K}$; those on the left for the upper curve,
 $T = 563.1^{\circ}\text{K}$. The circles are experimental values.

this theory, with 24 oscillators of a single frequency, and with the molecular heat and the diameter for collisional deactivation restricted to reasonable values.

When we attempt to use a model with two frequencies, the number of possibilities is greatly increased, since, instead of having only s and m to select arbitrarily for each model, we have now s , r , t , and m . Nor is it easy from the structure of the molecule to obtain information as to these values. One may argue somewhat as follows:

The center of the molecule is the group



and this group, since it is composed of four atoms, must have six vibrational degrees of freedom, all of which are presumably of rather low frequencies; then, to complete the molecule, we add six hydrogen atoms, each of which contributes three degrees of freedom; all of these are of high frequencies, since the carbon-hydrogen bond is very strong. Therefore we ought to take $s = 6$, $r = 18$, and $t = 3$ or 4. The value for t is of course a pure guess.

But this same argument may be used to reach a very different conclusion. It is true that the hydrogen-carbon bond is very strong, and hence the frequency of vibration in the direction of the line of centers will be high; but the vibration frequencies in the other two directions will not be affected by the strength of this bond. Therefore we should take $s = 18$, $r = 6$, and t whatever small integer we like.

It is evidently impossible to reach any definite conclusion from such arguments; it is probably better not to attempt to construct a definite correlation between the frequencies of the oscillators in our model, and the

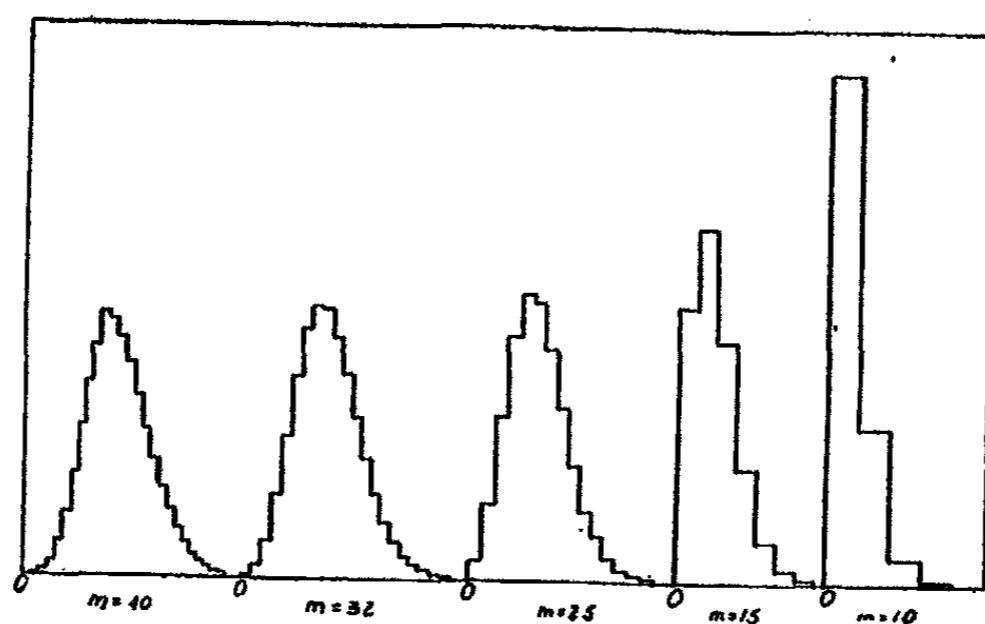


FIG. 4
Contributions of various quantum states to K_{∞} .

vibrations of the atoms in the actual molecule, until the structure of the actual molecule is far more definitely known than is the case at present. Putting aside these considerations, therefore, we will attempt to see how well the experimental data may be fitted when two frequencies are used for the oscillators.

It is found that when we take $s = 6$, $r = 18$, $t = 3$, $m = 25$, we must choose σ^2 as about 10^{-14} , which is reasonable, but that the curves at the two temperatures do not have sufficient spread. For this case the vibrational contribution (at 603.1°K .) to the molecular heat is 14.46 calories, and to the heat content, 3228 calories. With values as before, except that $t = 2$, the spread is increased slightly, though it is still not nearly enough, and the value necessary for σ^2 becomes about 10^{-15} . The contribution to the molecular heat is 23.28 calories, and to the heat content 5026 calories. Increase in the value chosen for m leads to rapidly increasing molecular heats and decreasing values for σ^2 . It is not possible to get good agreement with experiment by using six low frequencies, and eighteen high ones in the molecule.

If we decrease the number of high frequencies, the effect which they produce becomes smaller, and that of the low frequencies greater. Also, to keep the specific heat low enough, we have to take the high frequencies quite high, and the case is soon reached where they have no appreciable effect on the reaction. Reference to Table III shows how rapidly the heat content per

oscillator is decreasing when the frequency corresponds to a wave length of 5μ or less; for frequencies much higher than this, the effect of an oscillator would be entirely negligible. It is well known that all compounds containing the group CH_2 or CH_3 possess an absorption band near 3.4μ , and hence it is reasonable to suppose that there are some oscillators which may be neglected. It is quite possible that a satisfactory model could be obtained by neglecting six oscillators entirely, and assigning a single frequency to the remaining 18. Accordingly, equation (6) has been applied to the case $s = 18$, $m = 25$.

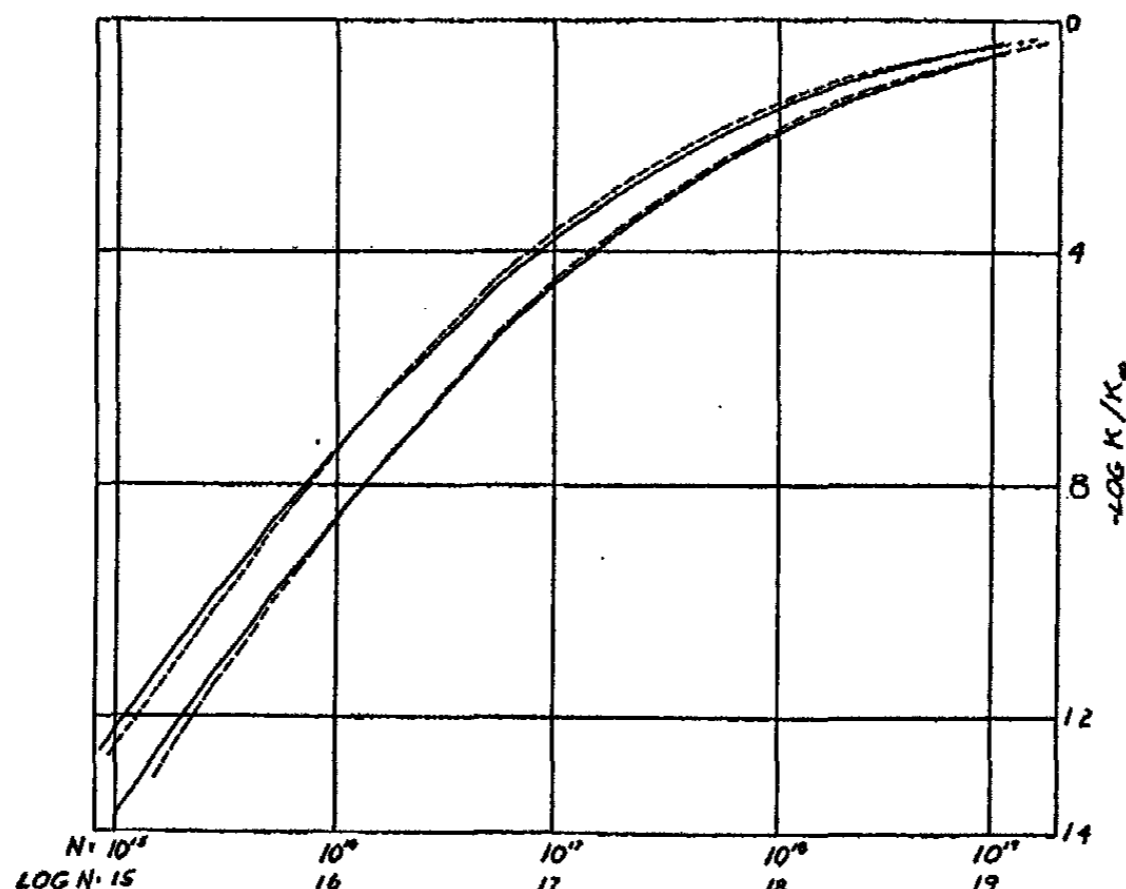


FIG. 5

— $s = 12$, classical
 - - - $s = 18$, $m = 25$

upper curves, 563.1°K .
 lower curves, 603.1°K .

The contribution to the molecular heat (at 603.1°K .) is 27.85 calories, and to the heat content, 7915 calories. When $\sigma^2 = 1.5 \times 10^{-14}$, the following results are obtained:

| N | Values of K/K_∞ | | | | |
|-----------|------------------------|-----------------------|-----------|-----------------------|-----------------------|
| | 603.1°K | 563.1°K | N | 603.1°K | 563.1°K |
| 10^{19} | .983 | — | 10^{16} | .414 | .490 |
| 10^{18} | .909 | .938 | 10^{15} | .173 | .223 |
| 10^{17} | .707 | .773 | 10^{14} | .0512 | .0708 |

When we take $\sigma^2 = 10^{-15}$, this gives almost exactly the same result as for 12 classical oscillators with $\sigma^2 = 1.5 \times 10^{-14}$. The theoretical curves for these two models are shown in Fig. 5. It has already been seen that the classical model with $s = 12$ is in fair agreement with experiment. This model, with eighteen oscillators of frequency corresponding to 13.57μ and six oscillators of high frequency, is in equally good agreement, and the associated values for the specific heat, the heat content, and the diameter for collisional deactivation are about as reasonable in one case as in the other.

To sum up the results which we have found for azomethane, we may say that if it is attempted to use oscillators of a single frequency, the selection of $s = 24$ leads to difficulties; for it is only possible to fit the results at both temperatures together by selecting a frequency which makes the molecular heat too great, and the target area too small; for $s = 18$, satisfactory results may be obtained by taking $m = 25$, which corresponds to a wave length of 13.57μ and to reasonable molecular heats and target areas; for $s = 12$, it is necessary to take the oscillators as classical, or nearly so, to keep the value of σ^2 reasonable, and then the molecular heat is plausible, but the heat content is rather large. For values of s less than 12, the results are not satisfactory. When oscillators of two different frequencies are used, it has not been found possible to obtain really good agreement except when one frequency is too high to have any appreciable effect. Thus by adding 6 oscillators of high frequency to the group of 18, or 12 to the classical group of 12, the total number is brought up to 24, the curves obtained are not appreciably affected, and the results remain satisfactory; the frequency of these oscillators need not be extremely high; a wave length of 3.4μ , which is always associated with the CH_2 group, is sufficiently short.

General Discussion

The introduction of quantum theory has lead to several interesting results. One of these is that for high enough frequencies, the dependence of K upon p becomes the same as is given by Rice and Ramsperger's Theory I; over the pressure which Hinshelwood and Thompson¹ have studied, the decomposition of propionaldehyde exhibits precisely this dependence. This would seem to suggest the possibility that here we have a substance with very few oscillators of moderately low frequency, although the experiments must be carried out at lower pressures for this to be certain. It is also very suggestive that, as may be seen from equation (6), and from the data in Table III, the transition from a monomolecular reaction to a bimolecular one takes place in a much smaller range of pressure when all the frequencies are rather high. It would be very desirable for someone to study the decomposition of propionaldehyde at pressures lower than 20 mm., which is as low as were used by Hinshelwood and Thompson; it ought to be possible to extend the measurements to .1 mm. without great difficulty, and perhaps much lower.

In the application to azomethane, the most satisfactory results have in general been obtained with values for σ^2 which do not exceed kinetic theory values, and which are possibly somewhat smaller; since the correct value for the molecular heat and the heat content is unknown, it is impossible to draw definite conclusions, but it would seem to be worth while to investigate the possibility that an activated molecule may survive a collision, its chance of survival depending upon various factors, such as its energy, the energy of the colliding molecule, the relative velocity at time of collision, and similar influences. It would seem very difficult to treat such a problem quantita-

¹ Hinshelwood and Thompson: Proc. Roy. Soc., 113 A, 221 (1926).

tively, but if it is found that every collision does not destroy an activated molecule, then such considerations cannot be neglected entirely. There is another advantage which might arise from such a treatment; if the average chance of destruction of an activated molecule at a collision increased with the temperature (presumably due to the increasing force of the collisions) the spread between theoretical curves at different temperatures would be decreased, while if this chance decreased as the temperature increased (due to the greater energy of the colliding molecules, and hence the greater chance for an activated molecule when the energy is statistically redistributed) the spread would be increased. If this latter factor were the dominant one, the experimental data for azomethane could be more easily interpreted.

With respect to nitrogen pentoxide, the theory in its present form is not quite sufficient. If the explanation of the maintenance of rate in this reaction is to be found in large diameters, the evidence in support of such diameters will have to be more convincing than at present; if in the assistance of radiation, experimental evidence would seem desirable, although should the active region be in the far infra-red, this may be almost impossible to obtain; if the solution is to lie in an abandonment of the First Law as applied to single elementary processes, this must come as a fundamental physical law; the necessity for such a change is at least suggested by various lines of evidence. It is, however, hard to see why, if this last explanation is the correct one, the decomposition of nitrogen pentoxide is unique. With respect to azomethane, it is possible to account for all of the experimental results, with fair accuracy, by the assumption of internal energy relationships which do not disagree with any of our very limited knowledge of the molecule of azomethane. The basic assumptions of the theory seem to be verified, but the results can undoubtedly be accounted for equally well by rather varied methods of development.

Summary

1. The theory of unimolecular reactions which the writer has previously suggested has been extended by the introduction of quantized degrees of freedom. The cases of quantum oscillators of a single frequency, and of two frequencies whose quotient is an integer, have been worked out, and the methods for more complex cases have been indicated

2. The decomposition of nitrogen pentoxide has been discussed, and it is shown that there is no longer any difficulty in accounting for the rate of this reaction at moderately high pressures; it is not quite possible in the present form of the theory to account for the complete maintenance of the rate at the lowest pressures studied, but the discrepancy is not large. The various ways in which the difficulty may be overcome have been discussed.

3. The theory has been applied to azomethane, and it is found that the results may be completely accounted for by assuming oscillators in such numbers and of such frequencies as to give reasonable values to the molecular heat and the internal energy, and that when this is done the value which must be assigned to the diameter for collisional deactivation is of the order of magnitude of kinetic theory diameters.

Pasadena, California.

A PREVALENT ERROR IN THE DERIVATION OF THE FREEZING-POINT AND BOILING-POINT LAWS FOR DILUTE SOLUTIONS

BY ARTHUR W. DAVIDSON

Introduction

The application of the classical methods of van't Hoff to the study of very dilute solutions no longer plays the vital part in physical chemistry that it held during the early days of this science, and it is entirely possible, now that more uniform and rigorous lines of development are available, that these older methods of approach to the problem may eventually become obsolete and possess interest for the chemical historian only. Nevertheless, the generalizations of van't Hoff are still quite widely used in the presentation of the colligative properties of dilute solutions in contemporary textbooks and treatises of physical chemistry, although they are not always correctly interpreted.¹ The author feels that it may yet be worth while to point out an error which has crept into two of the dilute solution derivations, and which still persists in several of the recent English and American texts.

The Freezing-Point Law for Dilute Solutions

This error occurs in the thermodynamic derivation of the freezing-point and boiling-point laws from the van't Hoff law of osmotic pressure. The methods used vary in detail, but are generally based on a reversible cyclical process similar to that originally employed by van't Hoff,² which process, for clarity, it will be necessary to describe briefly at this point. For freezing-point depression, the cycle may be outlined as follows. Start with a very large amount of a dilute solution, containing one gram mole³ of solute in V liters of solution, at the temperature T_0 , the freezing-point of pure solvent. (1) By means of a piston provided with a semi-permeable membrane remove isothermally and reversibly such an amount of solvent as contained one gram mole of solute.⁴ (2) Freeze the solvent so removed at T_0 . (3) Cool the solution and the now solid solvent, separately, to the temperature T , the freezing-point of the solution. (4) Melt (or dissolve) the solid solvent into the solution at T . (5) Warm the solution to T_0 .

In this cycle osmotic work is done upon the system, heat is evolved at T_0 , and a smaller quantity of heat is absorbed at the lower temperature T . If we represent by w the amount of work done upon the system and by q and

¹ This has recently been emphasized by Bancroft and Davis: *J. Phys. Chem.*, 32, 1 (1928), who discuss particularly the relation between osmotic pressure and vapor pressure.

² Van't Hoff: *Z. physik. Chem.*, 1, 481 (1887). The derivation in question occurs on pp. 496-497 of this article.

³ Van't Hoff used the kilogram mole and the kilogram calorie as units of mass and heat, respectively. In this discussion the gram mole and gram calorie are used, in conformity with modern practice; this has no effect whatever upon the point at issue.

⁴ Since the solution is dilute, the volume of this amount of solvent may be taken as V liters without appreciable error.

q_0 the quantities of heat absorbed at T and evolved at T_0 , respectively, then, according to the second law of thermodynamics we may write either¹

$$\frac{w}{q} = \frac{T_0 - T}{T} \quad (1) \quad \text{or} \quad \frac{w}{q_0} = \frac{T_0 - T}{T_0} \quad (2)$$

Now the only appreciable external work involved in the cycle is the osmotic work,² which, if we represent the constant osmotic pressure at T_0 by P , is PV , and this, according to the van't Hoff osmotic pressure equation for dilute solutions, is equal to RT_0 , where R is the gas constant; so that RT_0 may be substituted for w in either of the above equations. There remains only the interpretation of the quantities of heat q and q_0 , and it is here that the above-mentioned error, now to be discussed, has been made, although it does not occur in the original derivation.

Van't Hoff himself did not make any close analysis of the cycle which has just been described, but, after the briefest of outlines, immediately deduced the familiar equation for freezing-point depression, which may be written

$$\Delta T = \frac{RT_0^2}{ml_f} \quad (3)$$

in which ΔT is $T_0 - T$, the depression of the freezing-point, m is the mass of solvent in which one gram mole of solute is dissolved, and l_f is the heat of fusion per gram of solvent at T_0 .

In more recent discussions of the subject, however, it has been customary to describe and analyze each step of the cycle much more minutely than was done by van't Hoff, and confusion, rather than increased clarity, has resulted. For the statement is generally made that $q_0 = ml_f$. But inspection of the cycle shows quite plainly that q_0 must include not only the heat evolved when the solvent freezes, but also the heat given out during the removal of the solvent by osmotic work.³ This fact, which, it seems to the writer, is essential to the correct interpretation of the cyclical process, appears to have been uniformly overlooked. Since the internal energy of the system under consideration is unchanged by removal of solvent, all of the external work done upon the system must be changed into heat which is given up to the surroundings. For this reason, q_0 is not equal to ml_f , but is $ml_f + w$, or $ml_f + RT_0$. At T , however, the only heat absorbed is that used in the melting of the solid solvent, so that the usual procedure of stating (or tacitly assuming) that

¹ The quantities of heat evolved in step (3) and liberated in (5) are nearly the same and are disregarded by van't Hoff; they would obviously be identical if the specific heats of the solvent in the solid and the liquid states were the same.

² The minute amounts of work due to changes in volume on freezing and melting may be disregarded without appreciable error.

³ This additional heat effect is not to be confused with heat of dilution, which would be negligible in a dilute solution.

$q = ml'_f$ (where l'_f is the heat of fusion per gram at T),¹ is entirely correct. But the supposition that q_0 is greater than q only because l_f is greater than l'_f is altogether erroneous.²

Returning to equations (1) and (2), it is evident from the foregoing discussion that we may write

$$\frac{RT_0}{ml'_f} = \frac{\Delta T}{T} \quad (4)$$

but that it is *not* correct to say that $\frac{RT_0}{ml_f} = \frac{\Delta T}{T_0}$, as is done in many textbooks,³ although we might say⁴

$$\frac{RT_0}{ml_f + RT_0} = \frac{\Delta T}{T_0} \quad (5)$$

Equation (4) may be written

$$\Delta T = \frac{RT_0 T}{ml'_f} \quad (6)$$

In order to reduce this to the familiar expression for freezing-point depression in dilute solutions, two assumptions are necessary, both of which are valid for dilute solutions. First, T_0 and T must be so close together that $T_0 T$ is practically equal to T_0^2 . Second,⁵ l'_f must be equal to l_f . When these as-

sumptions are made, equation (6) becomes $\Delta T = \frac{RT_0^2}{ml_f}$, or when $m = 1000$ grams and R is taken as 2 calories,

$$\Delta T_m = \frac{0.002 T_0^2}{l_f}$$

¹ Strictly speaking, l'_f is the differential heat of solution rather than the heat of fusion, but in a very dilute solution these may be considered identical.

² As a matter of fact, the heat of fusion does generally increase with increasing temperature, since the specific heat of a substance is generally somewhat higher in the liquid than in the solid state. But this difference, for a small temperature interval, will always be exceedingly minute (and will, in fact, be balanced by the minute difference between the amounts of heat involved in steps (3) and (5) above); for some substances it may even be 0. In any case, the difference between l_f and l'_f is in no way essential to the derivation, for it is obvious that if it were zero for any particular solvent the validity of the freezing-point equation would not be impaired in the slightest degree; on the contrary, the derivation would then be more rigorous. In a cycle such as that described, however, the amount of heat evolved at the higher temperature must be greater than that absorbed at the lower, and the change in heat of fusion with temperature comes readily to mind. That is probably why the real difference between q_0 and q has apparently escaped attention hitherto.

³ See, for instance, Walker: "Introduction to Physical Chemistry," 423 (1922); Taylor: "Treatise on Physical Chemistry," 1, 277 (1925); Taylor: "Elementary Physical Chemistry," 252 (1927).

⁴ Since the solution is dilute, m is a large quantity, and the amount of heat evolved in freezing the solvent is a much larger quantity than RT_0 . On this account, no serious numerical error is introduced by using ml_f instead of $ml_f + RT_0$. It seems to the writer, however, that this omission ought to be pointed out explicitly as an approximation, otherwise the theoretical defect is sure to be puzzling to students and likely to cause further confusion, as will be shown below.

⁵ This second assumption has really been made at an earlier stage, since the amounts of heat involved in steps (3) and (5) of the cycle have been considered equal to each other. This implies that the specific heats of solid and liquid are the same, in which event the heat of fusion is independent of temperature. It may be pointed out here also that if $l'_f = l_f$, equation (5) can be obtained from (4) by a simple algebraic transformation.

which is the form in which the equation is generally used, ΔT_m being the molal freezing-point depression.

The Boiling-Point Law for Dilute Solutions

The same oversight occurs in most of the texts which describe in detail a cyclical process for the derivation of the boiling-point law for dilute solutions, even though in this case it produces rather serious complications. This derivation does not appear in the original van't Hoff article, but can readily be made by means of a cycle exactly analogous to that used at the freezing-point. This may be briefly outlined as follows. Start with a very large amount of a dilute solution, containing one gram mole of non-volatile solute in V liters of solution, at T_0 , the boiling-point of pure solvent. (1) By means of an osmotic piston remove V liters of solvent as before. (2) Evaporate the solvent at T_0 ; (3) Warm the solution and now gaseous solvent to T , the boiling-point of the solution; (4) condense the solvent back into the solution at T , and then (5) cool the solution to T_0 . In this cycle osmotic work is done upon the system, heat is absorbed at T_0 , and a *larger* amount of heat is liberated at the higher temperature T . We may then write¹

$$\frac{w}{q} = \frac{T - T_0}{T} \quad (7) \quad \text{or} \quad \frac{w}{q_0} = \frac{T - T_0}{T_0} \quad (8), \text{ where}$$

q and q_0 are the quantities of heat evolved at T and absorbed at T_0 , respectively.

The net external work done upon the system is the osmotic work PV , which is equal as before to RT_0 . The usual statement that $q_0 = ml_v$ (l_v being the heat of vaporization per gram of solvent at T_0) is erroneous. *Heat is given out during the osmotic removal of solvent in an amount equivalent to the osmotic work done upon the solution.* The net amount of heat absorbed at T_0 is therefore $ml_v - RT_0$. It is, however, correct to say that $q = ml'_v$, where l'_v is the heat of vaporization at T .

We may now assume, as before, that for a short temperature interval l_v and l'_v are equal; then ml'_v is obviously greater than $ml_v - RT_0$, which is in accord with the laws of thermodynamics. But if we were to fail to take into account the heat equivalent of the osmotic work, and make the same assumption as to the independence of l_v upon temperature, we should find no difference between q and q_0 , which would involve a violation of the first law, since work has been done upon the system. Or if, recognizing that q must be larger than q_0 , we were to attempt to attribute this difference to the change in heat of vaporization with temperature, we should find ourselves in a still more embarrassing predicament, in that the heat of vaporization

¹ As before, the amounts of heat involved in steps (3) and (5) are nearly the same, and the difference between them may be disregarded without error if the temperature interval is small. They would be identical if the specific heats of the solvent at constant pressure in the liquid and the vapor states were the same, but of course this is never actually the case. Also, it should be noted that work is done by the system in the evaporation of the solvent and the expansion of its vapor, which is balanced by the practically identical amount of work done on the system in the condensation of the solvent.

always actually *decreases* with increasing temperature, so that l'_v could not possibly be greater than l_v . Nevertheless, exactly this error has been made in several widely-used text-books of physical chemistry.¹

Returning to equations (7) and (8), it is evident that, calling the boiling-point elevation ΔT , we may formulate the boiling-point equation as follows

$$\frac{RT_0}{ml'_v} = \frac{\Delta T}{T} \quad (9) \quad \left(\text{not } \frac{RT_0}{ml_v} = \frac{\Delta T}{T_0} \right)$$

Making the same approximations for a dilute solution as in the case of the freezing-point law, equation (9) becomes

$$\Delta T = \frac{RT_0^2}{ml_v}$$

or, when $m = 1000$ grams,

$$\Delta T_m = \frac{0.002 T_0^2}{l_v}$$

which is the familiar form of the boiling-point law for dilute solutions, ΔT_m being the molal boiling-point elevation.

It is admitted that the equations which have here been criticized² lead to the same results as the correct ones, and, for that matter, are approximately true for dilute solutions and would become exactly true at infinite dilution. But it is the writer's contention that these equations contain an error in reasoning which is likely not only to lead to serious contradictions such as those which have been pointed out above, but also to encourage adverse criticism of the use of the reversible cycle for deriving thermodynamic equations, in spite of the simplicity of this method.³

The Freezing-Point Law for Ideal Solutions

In conclusion, it may be pointed out that, by means of a slight modification of the van't Hoff cycle, it is possible to derive the approximate integral form of the freezing-point equation for ideal solutions (the so-called Schroeder-

¹ For instance, in W. C. McC. Lewis: "System of Physical Chemistry," 2, 129 (1920), where a similar, though not identical, cycle is described, it is definitely stated that the heat given out in condensation at a lower temperature is less than that absorbed in evaporation of the same quantity of solvent at a higher. Also, in Taylor: "Treatise on Physical Chemistry," 1, 276 (1925), where another similar cycle is described by Frazer, we find the statement that the osmotic work is equal (in the notation here used) to $ml'_v - ml_v$. Here, again, the value of l_v is incorrectly supposed to increase with increasing temperature, and the attempt to equate the osmotic work to $ml'_v - ml_v$ leads to the rather serious discrepancy that heat is represented as being absorbed at a higher temperature, work done upon the system, and a smaller quantity of heat liberated at a lower temperature, which is obviously impossible in a reversible cycle. (There are several other defects in this particular cycle, which, however, have no immediate bearing upon the point at issue. It is reproduced unchanged in Taylor: "Elementary Physical Chemistry," pp. 250-251 (1927)).

² That is, $\frac{RT_0}{ml_t} = \frac{\Delta T}{T_0}$ and $\frac{RT_0}{ml_v} = \frac{\Delta T}{T_0}$

³ See Washburn: J. Am. Chem. Soc., 32, 468 (1910).

Le Chatelier equation) in a very simple and direct manner. Since the writer has not been able to discover this method of derivation in any of the standard reference works, and it has apparently not been described anywhere in the literature of the subject, it will be outlined briefly here.

Start with a very large amount of an ideal solution of any concentration, at T_0 , the freezing-point of pure solvent. (1) By means of an osmotic piston, remove isothermally and reversibly one gram mole of solvent, the volume of which we shall denote by V_0 . (2) Freeze this solvent at T_0 ; (3) cool the solution and solid solvent to T , the freezing-point of the solution, (4) melt the solid into the solution at T , and then (5) warm the solution to T_0 . Let us suppose that the specific heats of the solvent are the same in the solid and the liquid states;¹ in that case the amounts of heat involved in steps (3) and (5) are equal, and need not be considered further. Also, in such a case, the differential molar heat of solution of the solvent, in an ideal solution, will be independent of temperature and equal to the molar heat of fusion of the solvent, which we shall call L_f . Since the work done upon the system is PV_0 , we may write

$$\frac{PV_0}{L_f} = \frac{T_0 - T}{T} \quad (10)$$

Now, for an ideal solution, $PV_0 = -RT \ln x$, x being the mole fraction of solvent, so that in this case we may substitute $-RT_0 \ln x$ for PV_0 . Making this substitution we get from equation (10)

$$\frac{RT_0 \ln x}{L_f} = \frac{T - T_0}{T}, \text{ or } \ln x = \frac{L_f}{R} \left(\frac{T - T_0}{T T_0} \right) \quad (11)$$

Here, of course, we may not assume that $T_0 T = T_0^2$, since the solution is not necessarily dilute. Equation (11) may be written

$$\ln x = \frac{L_f}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)$$

which is the familiar approximate integral form of the freezing-point equation for ideal solutions.

This method could not very well be used for the derivation of the boiling-point equation for ideal solutions, since the change of heat of vaporization with temperature could hardly be neglected.

Summary

1. An error which has commonly been made in the derivation of the freezing-point and boiling-point laws for dilute solutions by the method of van't Hoff has been pointed out, and the correct application of this method has been discussed.

2. It has been shown how a similar method can be used for the derivation of the approximate form of the freezing-point equation for ideal solutions.

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¹ This assumption always has to be made in deriving the Schroeder-Le Chatelier equation, whatever method is used.

OSMOTIC PRESSURES OF CONCENTRATED SOLUTIONS

BY JOEL H. HILDEBRAND

Two recent papers by W. D. Bancroft and H. L. Davis¹ upon the above topic, have presented a number of interesting points, certain of which seem to me worthy of further comment, especially in view of the fact that these papers appear to have been inspired, to some extent, by certain statements concerning osmotic pressure contained in my monograph on "Solubility."² The authors discuss at length the derivation of the equation concerning osmotic pressure with vapor pressure, paying particular attention to the question of whether the volume to be used is that of the solution or of the pure solvent. They seem to regard this equation as the basis essential to the building of a sound theory of concentrated solutions, saying that since this equation "applies to all solutions and is absolutely accurate, except for the specified limitations, we must start from it as a base." Now it was pointed out a number of years ago by Washburn³ that the various colligative properties of solutions, which include osmotic pressure, vapor pressure, distribution coefficients, changes in freezing and boiling points, electrode potentials, etc., can all be connected in pairs by thoroughly rigid thermodynamic equations which involve no theory of solutions. The correct equations, at least the more important of them, have already been derived by various competent persons and I do not wish to go further into these derivations, but rather to re-emphasize that although these equations permit the calculation of one colligative property from another, they do not serve to calculate such a property from the properties of the pure components and the composition of the mixture. Except in the cases, therefore, where one colligative property has been experimentally determined, it is necessary in the calculation of another to invoke some relationship with composition, which is extra-thermodynamic, and which will, in general, depend upon the specific substances making up the solution. The equation which Bancroft and Davis insist upon as the starting point in a theory of solution belongs in the former category. The van't Hoff equation giving osmotic pressure by a gas law equation, and Raoult's law connecting vapor pressure with composition belong in the latter category, and it is not possible to go from the former to the latter by a simple logical process or by the aid of thermodynamics alone.

It is interesting to note that Bancroft and Davis admit the validity of Raoult's law for many systems throughout the entire range of composition. They appear to be unwilling, however, to accept the full thermodynamic consequences. Although all of the equations connecting other colligative properties with composition can be derived from Raoult's law by the aid of thermodynamics alone, these writers, along with writers of most textbooks

¹ Z. physik. Chem., 130, 626 (1927); J. Phys. Chem. 32, 1 (1928).

² Hildebrand: "Solubility," (1924).

³ J. Am. Chem. Soc., 32, 653 (1910).

on physical chemistry, seem to regard osmotic pressure as somehow having a more fundamental significance than the other means of measuring escaping tendency. Now the escaping tendency of one component of a solution may be measured by any process which can serve to separate this component reversibly from the solution. These processes include not only the escape through a semi-permeable membrane into the pure liquid, but also the escape into the vapor phase, into the solid phase, into another solvent immiscible with the first; or, in the case of substances easily oxidized or reduced, the escape to or from electrodes. Not all of the above are equally simple, but there is nothing about any one of them, such as osmotic pressure, which makes its selection a matter of necessity. It seems hard to understand, therefore, why Raoult's law, $p_1 = p_1^\circ n_1$, if accepted, should be mutilated by combination with an inaccurate osmotic pressure equation into a relation such as $\ln(p_1^\circ/p_1) = n_2/n_1$ (the notation used here is that adopted in my monograph), which has no advantage over Raoult's law and less accurately describes actual systems. Of this equation, the authors say that "it is a relation fundamental to the determination of molecular weights from freezing points or boiling points of solution." They seem not to realize that Raoult's law serves the same purpose.

When these authors state that Raoult's law "has as yet no theoretical explanation," they overlook the simple yet no less convincing explanation which I have given¹ and which is also implicit in an earlier statement of Washburn.²

Bancroft and Davis take exception, furthermore, to the designation by G. N. Lewis and myself of the equation $PV = RT$ (V denoting the volume of solution containing one mol of solute) as the van't Hoff equation for osmotic pressure. They say: "The above discussion will also throw light on another objection made to what Lewis calls the van't Hoff equation. Hildebrand recently expressed this objection on the ground that 'it leads to absurd figures, for, as the proportion of solvent in the solution approaches zero, the osmotic pressure actually approaches infinity, while according to the equation of van't Hoff it should never exceed a few hundred atmospheres.' Hildebrand is making the common mistake of substituting V the volume of the solution in which one gram molecular weight of the solute is dissolved for what we have called V_1 , the volume of the solvent in which one gram molecular weight of the solute is dissolved. The two are identical for infinitely dilute solutions, but not necessarily so for any other concentration. For the concentrated solutions V_1 becomes infinitely small and P therefore may go to infinitely large values. It should be clearly understood, however, that an equation of the form $PV = RT$ cannot accurately express osmotic pressures over any wide range of concentrations, no matter what definition be given the V . If V_1 be used instead of volume of solution, the range is increased and the error is readily calculable for the ideal solution."

¹ J. Am. Chem. Soc., 38, 1453 (1916); "Solubility," 24 (1924).

² Trans. Am. Electrochem. Soc., 12, 333 (1912).

I regret if I have given the impression that van't Hoff was unaware of the limitations upon the above equation. No one familiar with the care with which these limitations were stated by van't Hoff himself can accuse him of ignorance on this point. It is perfectly evident that van't Hoff never regarded the gas law equation as applicable to concentrated solutions. The fact is, however, that he lumped all deviations from it into the famous "van't Hoff ϵ ", and that the volume used by him, as well as by the textbook writers who have used this equation in deriving various physico-chemical formulae, is the volume of the solution rather than that of the solvent. It seems not unfair, therefore, to refer to it as the van't Hoff equation. In rejecting it as a basis for a theory of concentrated solutions, one accuses of ignorance, not van't Hoff, but those who continue to apply this formula to concentrated solutions at a time when a far better treatment is possible.

It may be pointed out, in conclusion, that while the application to osmotic pressure of an equation of the van der Waals' type by Bancroft and Davis naturally improves matters numerically by the introduction of two constants which can be empirically manipulated, the result can have little theoretical significance. If a really rigorous application of van der Waals' theory is desired, one should refer to the writings of van der Waals¹ himself and to those of Kohnstamm² and van Laar.³

¹ Z. physik. Chem., 5, 133 (1890); "Continuität," II, 146 ff.

² Z. physik. Chem., 36, 41 (1901); 75, 527 (1910).

³ Z. physik. Chem., 72, 723 (1910); 83, 599 (1913). "Sechs Vorträge über das thermodynamische Potential," (1906).

THE SOLUBILITY OF POTASSIUM BROMIDE IN ACETONE AS
RELATED TO THE INTER-IONIC ATTRACTION THEORY*

BY A. L. ROBINSON

In recent years an explanation of the anomalous behavior of strong electrolytes has been sought by use of the assumption of complete ionization and a calculation of the electrical inter-ionic forces. The treatment of Debye and Hückel¹ is based on a few fundamental physical principles and seems to be the most satisfactory in the region of very dilute solutions.

They find the activity coefficient of any ion to be given by

$$\log f_i = - \frac{Az_i^2(\sum c_i z_i^2)^{0.5}}{R(DT)^{1.5}}, \quad A = e^2 N^2 (\pi/R)^{0.5} \quad (1)$$

where f_i is the activity coefficient of the ion of the i th kind, z_i is its valence, R is the gas constant, D is the dielectric constant of the solution, T is the absolute temperature, e is the elementary electrical charge, and N is Avogadro's number. For water at 25°C., using ordinary logarithms and the dielectric constant of the pure solvent, and expressing all concentrations in moles per liter,

$$\log f_i = -0.357 z_i^2 (\sum c_i z_i^2)^{0.5} \quad (2)$$

The expression contains no empirical constants and gives the ideal or limiting behavior of ions which are regarded as point charges. The treatment of real solutions requires the introduction of a factor which depends on the sizes of the different kinds of ions, or their apparent diameters in solution, and another term which expresses the change in the dielectric constant of the solvent caused by the solute ions.²

Boiling point, freezing point, and solubility measurements can be employed as direct tests of this theory. It can easily be shown that

$$\log \left(\frac{S}{S_0} \right) = 0.357 (\sum (c_i z_i^2)^{0.5} - \sum (c_0 z_0^2)^{0.5}) \quad (3)$$

where S_0 is the solubility of a relatively insoluble salt in pure water and S is the solubility of the same salt in the same solvent containing other strong electrolytes in varying concentrations. By plotting the values of $\log S/S_0$ against corresponding values of the ionic strength ($\mu = 1/2 \sum c_i z_i^2$) a straight line should be obtained, for solutions sufficiently dilute, and the slope of the line should be $\frac{e^2 N^2 (\pi)^{0.5}}{(R DT)^{1.5}}$. Numerous solubility data collected by Noyes³,

* Contribution from the Department of Chemistry, University of Pittsburgh.

¹ Physik. Z., 24, 185; 334 (1923).

² Physik. Z., 26, 193 (1925).

³ J. Am. Chem. Soc., 45, 1098 (1924).

and particularly the work of Brønsted and LaMer¹ seem to have verified (3) as the limiting expression. The validity of the $(DT)^{1.5}$ factor, which expresses directly the electrical cause of the variation of the activity, has been tested in several instances, notably by Baxter², who measured the solubility of silver iodide in water, and water containing other salts, at 75°C, and found good agreement with (3).

The purpose of this investigation was to attempt another verification of the correctness of the $(DT)^{1.5}$ factor by making solubility measurements in a solvent whose dielectric constant differed from that of water by a considerable amount. The solvent used was acetone and potassium bromide was the saturating salt.

Materials and Methods

Ordinary acetone was refluxed over potassium hydroxide, distilled, dried over fused calcium chloride and then over sodium amalgam, distilled again, and the fraction boiling at $56.1^{\circ} \pm .04^{\circ}\text{C}$. (760 mm.) collected for use

The salts used were purified by at least five recrystallizations, including a crystallization from acetone, and careful drying, and were analyzed for purity. They were kept in small weighing bottles over phosphorus pentoxide.

The solutions were made up by adding amounts of the purified salts from the weighing bottles to the acetone contained in a calibrated flask. This operation was carried out, as far as possible, in a dry atmosphere

The solubility apparatus is shown in Fig. 1. A is a 500 cc. Pyrex flask from which the neck has been removed. B is a ground-glass joint and C is a mercury seal. D is the stirrer. E is another ground-glass joint and F is the siphon for removing the saturated solution. L is a calibrated (300 cc.) Pyrex Erlenmeyer flask with a constricted neck for marking. L is contained in a can R, into which thermostat water can be run while the saturated solution is being withdrawn. The open end of F is covered with several thicknesses of closely woven linen (previously digested with acetone) fastened with a platinum wire. G is a three-way stop cock; the first portion of the saturated solution drawn over thru F may be discarded thru H. K is a short piece of rubber tubing. The solubility measurements were made in a thermostat whose temperature could be controlled to 0.01°C ; all measurements were made at 25°C .

After completion of a run, which lasted for at least 40 hours, the saturated solution was drawn over into L. All the acetone except a few cc. was distilled off on a water bath and the solutions were diluted with conductivity water. The bromides and iodides were precipitated together with acidified silver nitrate and weighed as total silver halide. From this weight was subtracted the weight of the solvent halide (calculated from the known composition of the solution and the volume of the sample of saturated solution), giving the weight of the AgBr corresponding to the amount of KBr dissolved. When the barium salts were used as solvents a direct determina-

¹ J. Am. Chem. Soc., 46, 555 (1924).

² J. Am. Chem. Soc., 48, 615 (1926).

tion of the barium ion was made and the filtrate was analyzed for total halogen content. This permitted a check and gave assurance that the concentration of the solvent salt did not alter during the process of saturation

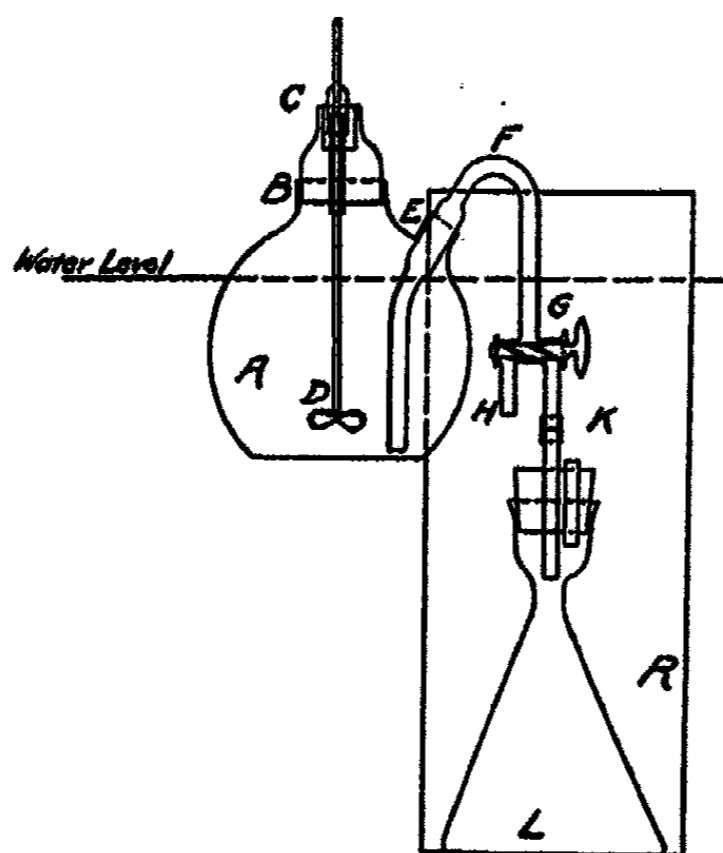


FIG. 1

TABLE I

| Conc. of solvent salt in equivs./liter | S equivs./lit. $\times 10^4$ | Ionic Strength moles/liter μ | $\sqrt{\mu}$ | S/S ₀ | log S/S ₀ |
|----------------------------------------|------------------------------|----------------------------------|--------------|------------------|----------------------|
| Solvent, acetone | | | | | |
| .00000 | 3.69 | .000369 | .0193 | 1.000 | .0000 |
| Solvent, NaI | | | | | |
| .000382 | 4.18 | .000800 | .0283 | 1.133 | .0542 |
| .000939 | 4.94 | .001436 | .0397 | 1.344 | .1284 |
| .001849 | 5.71 | .002421 | .0492 | 1.549 | .1899 |
| .003542 | 6.57 | .004199 | .0648 | 1.780 | .2503 |
| Solvent, KI | | | | | |
| .000343 | 4.14 | .000620 | .0249 | 1.121 | .0496 |
| .000877 | 4.89 | .001096 | .0331 | 1.323 | .1216 |
| .001763 | 5.79 | .001936 | .0440 | 1.567 | .1952 |
| Solvent, BaI ₂ | | | | | |
| .000137 | 4.24 | .000630 | .0251 | 1.149 | .0602 |
| .000408 | 5.10 ₅ | .001123 | .0335 | 1.381 | .1403 |
| .001206 | 6.23 | .002424 | .0493 | 1.686 | .2268 |
| Solvent, BaBr ₂ | | | | | |
| .000240 | 4.30 | .000686 | .0262 | 1.165 | .0663 |
| .000730 | 4.82 | .001290 | .0359 | 1.303 | .1152 |
| .001206 | 5.31 | .002421 | .0492 | 1.483 | .1578 |

and sampling. Due to the very small solubility of the KBr and the low concentrations of solvent salts used, duplicate runs often gave results discordant to 5%, but the increased solubility of the KBr in the presence of the added salts was so great that the general tendency of the solubility curves could be located without difficulty.

The first column of Table I gives the concentration of the solvent salt in equivalents per liter. The second column gives the solubility of the KBr in equivalents per liter calculated from

$$S = (K^+)(Br^-)^{\frac{1}{2}}$$

This will include cases of solvents containing no ions common to the saturating salt (heterionic solvents) as well as solvents containing ions common to the saturating salt (homoionic solvents) as Brønsted¹ has pointed out. The third column gives the ionic strength. The other column headings are self-explanatory. S_0 is the solubility in acetone alone.

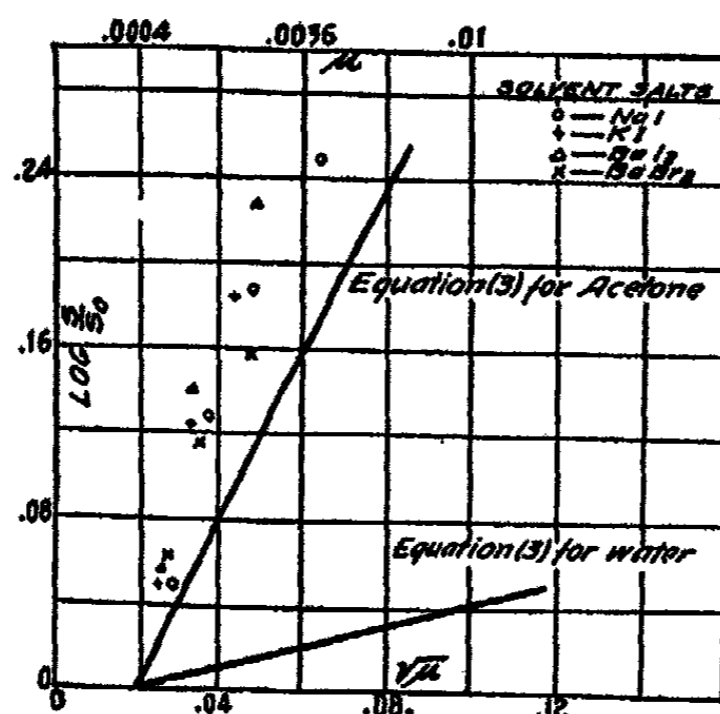


FIG. 2

Discussion of Results

A plot has been made of $\log S/S_0$ against the square root of the ionic strength $(\frac{1}{2}c_i z_i^2)^{\frac{1}{2}}$. Lewis and Randall², from a study of available data, had derived an empirical principle which stated that in dilute aqueous solutions the activity coefficient of a largely ionized salt is the same in all solutions in which the value of $c_i z_i^2$ summated for all the kinds of ions present, is the same. For the one-half of this quantity they suggested the name 'ionic strength'. The theoretical significance of this quantity is clearly shown by the theory of Debye and Hückel, which requires that the solubility of such a salt (the solubility is inversely proportional to the activity coefficient) shall be directly proportional to the square root of the ionic strength of the solution, provided the dilution be sufficiently great to consider the ions as point charges. The

¹ J. Am. Chem. Soc., 42, 761 (1920).

² J. Am. Chem. Soc., 43, 1112 (1921).

straight line to be expected from the theory, as well as the theoretical line for the behavior of a uni-univalent salt (such as the one investigated) in aqueous solution, is indicated in Fig. 2. The great difference in the slope of the two lines is to be attributed entirely to the different dielectric constants of the solvent media, the slope varying inversely as the three-halves power of this constant.

For all the solvent salts there is evidently some general agreement with the requirements of the theory. The solubility increases in acetone should be $\left(\frac{78}{20}\right)^{1.5} = 7.7$ times the increments for the same type of salt in water solutions with the same added salt concentration. The solubilities found are all somewhat greater than those demanded by the theory. It is suspected that the presence of a constant trace of water in the acetone used may be responsible for at least a part of this difference. Solvent salts of two valence types, and both homoionic and heterionic solvents, produce approximately the same increase in solubility at the same ionic strength.

Summary

The solubility of KBr in acetone and in acetone solutions of two uni-univalent and two bi-univalent salts has been determined up to an ionic strength of .004M. Large increases in the solubility of the KBr were found, of the magnitude to be expected from the theory of Debye and Hückel.

WILDIERS' BIOS

The isolation and identification of "Bios I"

BY EDNA V. EASTCOTT

In January 1925 there appeared under the title "The Bios Question" a much needed review by F. W. Tanner,¹ of the papers on bios which have appeared since Wildiers' announcement² in 1901 of a new substance indispensable to the (normal) development of yeast to which he gave that name; the review includes an account of some earlier work connected with the discussions which arose out of Wildiers' discovery, and closes with a bibliography of 144 titles.

In the paper by Wildiers on which so much subsequent work is based, he showed that when a solution containing sugar salts and water was inoculated with *Saccharomyces cerevisiae* I Hansen, there was very little reproduction of the cells, but that if a filtered decoction of yeast was added, the cells multiplied rapidly. To the (unknown) active constituent of the yeast decoction he gave the name Bios; he described its behavior with certain reagents, showed that it was dialysable, and proved that it was not present in yeast ash, urea, asparagine, etc. etc. The title of Wildiers' paper is "Nouvelle substance indispensable au développement de la levûre"; but in the paper itself the author does not claim that if bios be absent no reproduction at all will take place, but merely that in the absence of bios budding is very slow and the resulting cells are not healthy; if the word "normal" had been prefixed to "development" the title of his paper would have expressed its contents more accurately. Wildiers went on to show that the yeast decoction may be replaced by peptone, extract of meat, or beer wort; he expressed this fact by saying that all four substances contain "bios" which implies that the active principle in all four is the same, whereas it is obviously quite possible that more than one chemical substance may have the property suggested by the name. Recent work by Eddy and others, whose preparations differ markedly from our own, supports the latter view; and Fulmer³ obtained from alfalfa two extracts, differing in solubility, which were about equally potent in stimulating the reproduction of yeast.

A sketch of the circumstances which led to the study of bios being taken up in this laboratory and of the results obtained to date, was given by Professor Lash Miller in an address⁴ to the A. A. S. delivered in December 1923; this work has been continued, and progress reports have been published from time to time. The first results on which the rest depend were obtained by

¹ F. W. Tanner: The Bios Question. Chem. Rev., 1, 399-474 (1924).

² E. Wildiers: Nouvelle substance indispensable au développement de la levûre. La Cellule, 18, 313 (1901).

³ E. I. Fulmer and V. E. Nelson: Is bios a single substance? Proc. Iowa. Acad. Sci., 29, 371 (1922); see also J. Am. Chem. Soc., 46, 723-726 (1924).

⁴ W. Lash Miller: Wildiers' Bios. Science, 59, 197-199 (1924).

Dr. N. A. Clark,¹ who measured the rate of reproduction of the race of yeast with which all our work here has been done. When the cells were kept suspended by rocking in a malt infusion ("wort") at 25°C., their number doubled every 113 minutes, whether the initial seeding was with 5 cells per cc., or with larger numbers up to 8 million; this rate kept up unchanged until the alcohol formed by fermentation reached a concentration of 1.8 g. per 100 cc., which slowed it. Precisely the same rate of reproduction was observed in solutions of salts and sugar to which varying amounts of wort had been added; the rate at first was unaffected by the amount of wort, i.e. by the concentration of bios in the solution, but instead of continuing unchanged till slowed by alcohol, it suddenly fell almost to zero after an interval which increased with the amount of wort in the culture medium, and then the filtrate contained in Wildiers' sense "no bios."

Dr. Clark's experiments thus led to a convenient method for the quantitative determination of bios. Since the yeast crop shortly after normal reproduction ceases depends upon the amount of bios in the medium, it is sufficient to determine that crop; when this is known, Clark's curve of crop against wort content makes it possible to express the amount of bios in the medium in terms of that contained in one cc. of his wort. In applying this method it is not necessary to make determinations of the rate, for if the amount of bios present in the medium be not too great, the final crop will be reached in less than 24 hours; and as reproduction after the bios is used up is very slow, the 24-hour crop will do. If this should be too large, however, the experiment must be repeated with a smaller amount of the bios-containing constituent of the culture medium.

The second result on which our work is based was that obtained by Dr. G. H. W. Lucas² who found that if wort were precipitated by baryta in a solution containing alcohol, and the precipitate and filtrate were separately freed from baryta, neither preparation (with salts and sugar) gave much of a crop of yeast, i.e. neither contained much of Wildiers' bios; but that if both the preparations together were added to the sugar and salts solution, the crop obtained was almost as great as that obtainable from the original wort. Thus by this treatment Wildiers' bios can be separated into two constituents; to the one carried down by the baryta the name "Bios I" was given and to the other "Bios II". The amount of Bios I in the given extract can therefore be determined by measuring the crop of yeast obtained (under standardized conditions) when the extract is added to a solution of sugar and salts containing excess of Bios II, and comparing with the crop obtained when a standard solution of Bios I was used. Until the Bios I itself had been prepared in a state of purity, the results were, of course, not absolute but gave the amount of Bios I in terms of that contained in one cc. of the standard Bios I solution. The amount of Bios II in the extract can be determined in a similar manner.

¹ N. A. Clark: The rate of formation and the yield of yeast in wort. *J. Phys. Chem.*, 26, 42-60 (1922).

² G. H. W. Lucas: The fractionation of Bios, and comparison of Bios with Vitamins B and C. *J. Phys. Chem.*, 28, 1180 (1924).

My own work began in October 1922 with an examination of a large number of vegetable and animal extracts by this method (page 1099); among them tea dust seemed the best starting point for an attempt to prepare Bios I in purity, and in 1924 Mr. H. D. Sims and Mr. N. C. Cahoon worked up a large amount (p. 1104). Already in 1923 a few milligrams of a crystalline substance had been obtained which we now know to have been practically pure Bios I, and later Mr. Sims prepared some 20 g. of a powder we now know to contain 40% Bios I; this preparation constituted the supply of "Bios I" used as a reagent in most of the subsequent work in this laboratory, but illness hindered his attempt to isolate the pure substance.

In October 1927 I took over the material remaining from the work with tea; investigation showed that most of the Bios I was contained in some 8 liters of a black solution; this was treated as described on page 1105, and from it was obtained the crystalline Bios I which was analysed and identified as described below.

Technique

1) *Rocker-Tube*.—Much of the early work reviewed by Tanner was done in Erlenmeyer flasks or test tubes; under these conditions the yeast collects in a layer on the bottom of the vessel, many cells are denied free access to the nutrient medium, and as Dr. Clark found, the rate of reproduction is irregular. In all our work the cells were kept suspended by rocking the medium in an L-shaped tube¹ (closed at the bottom) immersed in the water of a thermostat at 25°C. A rack held 24 of these "rocker-tubes", and they were rocked 30 times a minute through an angle of 60 deg. in the plane of the L. To see whether the aeration thus provided was sufficient, some experiments were made where air was bubbled through the medium during the rocking, but this procedure proved to have no influence on the crop, and was discontinued.

2) *Sugar and Salts Solution (S & S)*.—Fulmer's² experiments on reproduction in a solution free from bios showed that under the conditions of his experiments and with the yeast employed by him the proportions in which the various salts are contained in the culture medium have a great influence on the crop. With solutions containing bios this factor is of minor importance; reducing the weights of all the salts by half, or varying the proportions within wide limits leaves the crop unchanged. The reagent solution we used contained 15 g. potassium dihydrogen phosphate, 7.5 g. cryst. magnesium sulphate, 30 g. ammonium nitrate, 2.5 g. calcium chloride hexahydrate and 360 g. sugar in 1800 cc. of solution; 5 cc. of this was used in the rocker-tube and made up to 10 cc. by the other ingredients of the culture medium.

The S & S solution is slightly acid and when it is repeatedly sterilized turns yellow-brown, if heated for a long time almost black; it then contains

¹ C. G. Fraser: Methylene-blue as indicator in determining the toxicity of phenol and phenol-salt solutions towards yeast. *J. Phys. Chem.*, 25, 1-9 (1921).

² E. I. Fulmer, V. E. Nelson and F. F. Sherwood: The effect of the composition of the medium on growth of yeast. *J. Am. Chem. Soc.*, 43, 191-199 (1921).

something toxic to the yeast. The S & S solution was therefore divided among a number of flasks, so that it was not necessary to sterilize any one of them too often.

3) *Reagent solutions of Bios I and of Bios II*:—Except where otherwise stated, these were prepared from malt-combings by the method described by Lucas; one cc. was used in the rocker tube. These reagents were not, of course, solutions of single chemically pure substances; it is only recently that the identity of Bios I has been established, and the methods for further purifying Bios II we now use had not yet been discovered. One cc. of the Bios I reagent with S S gave a yeast crop of about $C = 30$, with the chemically pure substance it is about $C = 25$; one cc. of the Bios II reagent gave a crop of about $C = 50$.

4) *Yeast culture*:—In the summary at the close of Tanner's "Bios Question" he says "One group of investigators denies the existence or need on the part of the yeast plant of a substance like 'bios' ". The unfortunate title chosen by Wildiers for his paper is responsible in part for this division of the investigators into groups; but there is another reason, which is that different races of yeast react very differently with bios. It is easy to obtain a culture which reproduces rapidly in our own sugar and salts solution by diluting it to half with water and inoculating from a Fleischmann's yeast cake, the races that need bios multiply very slowly, and those that do not soon constitute the dominant culture; and Lucas¹ has shown that a top-yeast from Professor Eddy's laboratory, while helped by the addition of bios, yet in the absence of that substance gave a much larger 36-hour crop than was obtained from the race used here when both Bios I and Bios II were added to the sugar and salts. If determination of the yeast crop is to be used as an analytical method for the quantitative determination of bios, it is therefore necessary to procure a strain of yeast which is as sensitive as possible to the presence of that substance; the following is the method employed here:—

Fifty cc. of wort² in a 250 cc. Erlenmeyer flask is inoculated with a piece about the size of a pin head from the centre of a Fleischmann's yeast cake and left 20 hours at 25°C. Two cc. are then pipetted into about 25 cc. sterile water and the number of colonies per cc. (usually 9 or 10 times 250,000) determined under the microscope (haemocytometer). This yeast suspension is then diluted with sterile water until each cc. contains from 10 to 20 colonies (a dilution of one to 50 thrice repeated usually serves), and one cc. of this dilute suspension is placed on the bottom of a sterile petri dish, covered with

¹ G. H. W. Lucas: loc. cit. p. 1095.

² *Wort*:—360 g of barley malt (ground in a coffee mill) is steeped in 1150 cc of water at 55°C. for 24 hours, the liquid is pressed out and filtered through paper, then autoclaved for half an hour at a steam pressure of 15 lbs, and let stand for 3 or 4 days at room temperature, during which time a muddy precipitate forms; this is filtered off, and the wort (sp. gr. 1.07) is sterilized for half an hour at 100°C. Before sterilizing, it is convenient to pipette a number of 50 cc portions into small Erlenmeyers (for use in maintaining the yeast culture) which may be plugged with cotton wool over which a piece of waxed paper is tied.

10 to 15 cc. of wort-agar¹ at 42°C., and mixed by rotating the dish. After 3 or 4 days at 25°C. the colonies are examined, and one selected that shows well marked prongs; a piece of this is put into 50 cc. of wort and the process repeated. Yeast from a pronged colony of the third plating is considered pure; it is grown in wort (Erlemeyer, 25°C.) and must be transferred every 24 hours to fresh wort, for if left longer the alcohol formed by fermentation will affect the properties of the yeast.²

When the culture media in the rocker-tubes are to be inoculated, one cc. is removed from the culture in wort and used to seed a fresh portion of 50 cc. of wort, thus maintaining the supply. The rest of the wort culture is then filtered with suction on a Buchner through filter paper sterilized by alcohol; the culture (suspension of yeast in wort) is poured slowly on the centre of the paper so that the yeast will be collected as much as possible in one place, and it is then washed on the paper with 50 cc. of sterile water added in small portions. A sufficient amount is then removed by a sterile glass spatula, and suspended in sterile water; the count is taken in the haemocytometer, and a dilute suspension prepared to contain from 10 to 20 times 250,000 cells per cc. One cc. of this is added to the 9 cc. of medium in each rocker-tube, which is thus seeded with a "Count" of 1 to 2.

5) *Determination of the yeast crop*:—At first the haemocytometer was used, but to get a fair result a large number of drops must be counted which takes much time. We then adopted Carlson's³ method of determining the volume of the yeast crop by centrifuging it into a narrow tube as in a phosphate determination. Before centrifuging the yeast must be treated with some chemical which will prevent fermentation, otherwise bubbles of gas appear in the column of yeast; Carlson's reagent was a one-percent sodium carbonate solution which shrinks the cells; at first we used a solution containing one-percent of phenol and 10-percent of sodium chloride which does not shrink them, but with some media this proved not toxic enough; later Miss E. M. Taylor introduced a solution of chloracetic acid (100 g. per litre) which we have used ever since.

To carry out the determination, 2 cc. of the chloracetic acid solution is pipetted into the centrifuge tube (the narrow tube stays full of air), the contents of the rocker tube are well mixed by shaking, 2 cc. is removed by a pipette and added to the chloracetic acid and stirred; the whole is then let stand 3 minutes and centrifuged 10 minutes at 1760 rev. per min. The three minutes delay is necessary to give time for the cells to shrink; longer delay or longer centrifuging does not affect the results if the yeast does not occupy more than 2 cm of the narrow tube. The centrifuge tubes are 11.5

¹ *Wort-agar*:—Agar-agar (14 g) broken into small pieces is covered with boiling water and let stand 3 or 4 hours in a covered crystallizing dish. Wort (700 cc) is then heated to boiling in an enameled saucepan, the agar is added, stirred, and brought to a boil, then filtered through cotton wool in a jacketed funnel, and collected in portions of about 10 to 15 cc in test-tubes. These are closed with cotton wool, and sterilized for half an hour at 100°C.

² E. I. Fulmer: The effect of alcohol on the toxicity of phenol towards yeast. *J. Phys. Chem.*, 25, 10-18 (1921).

³ T. Carlson: *Biochem. Z.*, 57, 313 (1913).

cm. long of which 5 cm. is the narrow tube; the inner diameter of the tube is about 1 mm.; there should be a sloping shoulder where the narrow tube joins the other, or yeast may stick there; the distance between the centre of rotation to the extremity of the narrow tube when in the centrifuge is 13 cm.

The height of the yeast column is measured by a millimeter rule; each tube is calibrated by means of the haemocytometer, and the number of cells is deduced from the height of the yeast column by means of a graph. This graph is constructed on the assumption that the cells are of normal size which was not the case with some of the plant and animal extracts; a drop from the rocker tube was therefore examined under the microscope, and the percentage of abnormal cells was determined; when this was large an empirical correction was made, the data for which were found by centrifuging cells whose appearance under the microscope was unusual. Even when all the cells were "bad" this correction never exceeded 10 percent.

The "Count" is the number of yeast cells appearing over a large square of the haemocytometer; a count of one ($C = 1$) corresponds to 250,000 cells per cc.; if the yeast crop is that from 10 cc. of medium, the number of cells in the crop is 2,500,000 times the "Count."

6) *Procedure*:—All glass apparatus was sterilized dry at 180°C.; 5 cc. of the S & S solution was pipetted into the rocker tube, then (if wanted) a measured volume of the Bios I or Bios II reagent, then the solution in which the bios was to be determined, water enough to bring the volume up to 9 cc., and finally one cc. of the yeast suspension used for seeding; this makes a total volume of 10 cc. with an initial Count of 1 or 2, i.e. from 2,500,000 to 5,000,000 yeast cells were used to seed the tube. After 24 hours rocking at 25°C., 2 cc. was pipetted into the chloracetic acid in the centrifuge tube and the yeast crop determined as described above.

Yeast Crops from Vegetable and Animal Extracts

Of the substances included in Table I, the fruit and vegetable juices were obtained by means of a glass lemon squeezer or by mincing, pressing, and filtering; in a few instances a little water was added. The infusions of grains, meals, etc., were prepared by pouring boiling water on the powdered material, letting stand 15 minutes, and filtering. The animal tissues were minced, stirred with water, let stand for a few hours and filtered through cloth; after which two volumes of alcohol was added, the precipitate filtered off and discarded, and the filtrate freed from alcohol and brought to the original volume with water. The number of cc. of water used in making up the extract, per gram of the substance extracted, is given under "water" in Table I.

With each of the extracts so prepared four determinations were made as described under "procedure," one cc. of the extract was used in each case; the yeast crops obtained are recorded in Table I, the unit is the "Count." The four were (a) the crop from the extract itself, (b) the crop from the extract with Bios I, (c) the crop from the extract with Bios II, (d) the crop from the extract with 0.5 cc. wort; and for each extract there was a fifth, viz: (e) the

TABLE I

| | Water | a | b | c | d | e | b-a | c-a | d-e |
|---------------------------|-------|-----|-----|-----|-----|-----|-----|-----|------|
| Orange juice | 0 | 288 | 275 | 430 | 570 | 282 | -13 | 142 | 288 |
| Grapes (juice) | 0 | 215 | 223 | 380 | 430 | 248 | 8 | 165 | 182 |
| Strawberry juice | 0 | 65 | 78 | 397 | 375 | 267 | 13 | 332 | 108 |
| Rhubarb juice | 0 | 160 | 144 | 270 | 270 | 340 | -16 | 110 | -70 |
| Beet juice | 0 | 140 | 220 | 200 | 380 | 304 | 80 | 60 | 76 |
| Turnip juice | 0 | 355 | 395 | 550 | 675 | 327 | 40 | 195 | 348 |
| Tomato juice (canned) | 0 | 474 | 490 | 484 | 680 | 270 | 16 | 10 | 410 |
| Horseradish | 2 | 19 | 19 | 20 | 17 | 340 | 0 | 1 | -323 |
| Mushrooms | 0.2 | 440 | 660 | 480 | 500 | 325 | 220 | 40 | 175 |
| Rice, polished | 4 | 41 | | 52 | | | | 11 | |
| Rice polishings | 6 | 221 | 310 | 214 | 420 | 245 | 89 | -7 | 175 |
| Rice starch | 6 | 20 | 22 | 33 | 356 | 340 | 2 | 13 | 15 |
| Maize | 6 | 98 | 108 | 195 | 330 | 248 | 10 | 97 | 82 |
| Corn Starch | 6 | 11 | 11 | 20 | 225 | 227 | 0 | 9 | -2 |
| Tapioca | 6 | 21 | 28 | 36 | 275 | 260 | 7 | 15 | 15 |
| Sago | 5 | 25 | 31 | 48 | 267 | 260 | 6 | 23 | 7 |
| Barley | 6 | 112 | 168 | 98 | 400 | 295 | 56 | -14 | -7 |
| Pot barley | 3 | | 144 | 346 | | | | | |
| Robinson's pat. barley | 3 | | 75 | 222 | | | | | |
| Malt extract | 12 | 245 | 250 | 335 | 430 | 193 | 5 | 90 | 235 |
| Malt combings | 6 | 237 | 335 | 265 | | | 98 | 28 | |
| Peas | 6 | 300 | 296 | 410 | 450 | 295 | -4 | 110 | 155 |
| Bran | 6 | 240 | 253 | 298 | 450 | 248 | 13 | 58 | 202 |
| Flax seed | 4 | 118 | 92 | 167 | 270 | 282 | -26 | 49 | -12 |
| Soy bean meal | 3 | | 494 | 790 | | | | | |
| Cotton seed meal | 6 | 385 | 387 | 510 | | | 2 | 125 | |
| Roman meal | 3 | | 309 | 350 | | | | | |
| Macaroni | 3 | 83 | 88 | 205 | 234 | 260 | 5 | 122 | -26 |
| Molasses | 9 | 215 | 260 | 268 | 415 | 390 | 45 | 53 | 25 |
| Tea | 6 | 143 | 165 | 322 | 450 | 248 | 22 | 179 | 202 |
| Tobacco stems, dried | 6 | 20 | 22 | 70 | 165 | 260 | 2 | 50 | -95 |
| Saffron, dried | 6 | 325 | 327 | 500 | 434 | 260 | 2 | 175 | 174 |
| Spinach | 0 | 165 | 205 | 170 | 365 | 195 | 40 | 5 | 170 |
| Lettuce | 0.6 | 118 | 128 | 348 | 320 | 270 | 10 | 230 | 50 |
| Alfalfa, dried | 6 | 103 | 115 | 168 | 170 | 238 | 12 | 65 | -68 |
| Catnip, dried | 6 | 230 | 235 | 330 | 374 | 270 | 5 | 100 | 104 |
| Lawn Grass | 12 | 100 | 97 | 140 | 290 | 295 | -3 | 40 | -5 |

TABLE I (Continued)

| | Water | a | b | c | d | e | b-a | e-a | d-e |
|-------------------------|-------|-----|-----|-----|-----|-----|-----|-----|------|
| Potato | 0 | 460 | 520 | 370 | 660 | 304 | 60 | -90 | 356 |
| Hyacinth, bulb | 2 | 150 | 165 | 270 | 350 | 262 | 15 | 120 | 88 |
| Hyacinth, roots | 2 | 50 | 50 | 200 | 290 | 245 | 0 | 150 | 45 |
| Gladiolus, bulb | 1.6 | 0 | 0 | 0 | 0 | 270 | 0 | 0 | -270 |
| Ginseng, dried | 6 | 250 | 210 | 250 | 350 | 340 | -40 | 0 | 10 |
| Onion | 0.3 | 0 | 0 | 0 | 0 | 282 | -0 | 0 | -282 |
| Dandelion flowers | 2.5 | 300 | 323 | 480 | 390 | 304 | 23 | 180 | 86 |
| Cloves | 6 | 77 | 75 | 122 | 240 | 248 | -2 | 34 | -8 |
| Pollen of lily | 3 | 95 | 102 | 265 | 310 | 267 | 7 | 170 | 43 |
| Cinchona bark, dried | 6 | 20 | 19 | 162 | 265 | 248 | -1 | 142 | 17 |
| Malt diastase | 500 | 9 | 6 | 28 | 287 | 304 | -3 | 19 | -17 |
| Trypsin | 200 | | 17 | 230 | 200 | 218 | | | -18 |
| Saliva | 0 | 30 | 28 | 42 | 320 | 265 | -2 | 12 | 55 |
| Klim | 8 | 125 | 129 | 177 | 262 | 335 | 4 | 52 | -73 |
| Egg white | 7 | 30 | 120 | 62 | 300 | 298 | 90 | 32 | 2 |
| Egg yolk | 7 | 108 | 164 | 148 | 390 | 298 | 56 | 40 | 92 |
| Buttermilk | 0 | 275 | 340 | 290 | 462 | 390 | 65 | 15 | 72 |
| Lemco | 12 | 233 | 230 | 805 | 260 | 304 | -3 | 572 | -44 |
| Peptone | 500 | 11 | 7 | 33 | 288 | 304 | -4 | 22 | -16 |
| Aminoids | 10 | 26 | 36 | 325 | 295 | 270 | 10 | 299 | 25 |
| Casein | 6 | | 28 | 22 | 285 | 218 | | | 67 |
| Ox kidney | 1 | 132 | 110 | 95 | 135 | 282 | -22 | -37 | -147 |
| Calf heart | 0.7 | 205 | 220 | 390 | 470 | 248 | 15 | 185 | 222 |
| Pig liver | 0.7 | 446 | 560 | 486 | 670 | 305 | 114 | 40 | 365 |
| Calf thymus | 0.8 | 135 | 143 | 242 | 315 | 248 | 8 | 107 | 67 |
| Ox pancreas | 0.6 | 150 | 170 | 280 | 370 | 305 | 20 | 130 | 65 |

TABLE Ia

| | d | a+e | diff | | d | a+e | diff |
|-----------|-----|-----|------|--------------|-----|-----|------|
| Orange | 570 | 570 | 0 | Malt extract | 430 | 440 | 10 |
| Grape | 430 | 463 | 33 | Bran | 450 | 488 | 38 |
| Turnip | 675 | 682 | 7 | Spinach | 365 | 360 | 5 |
| Tomato | 680 | 744 | 64 | Egg, yolk | 390 | 406 | 16 |
| Rice pol. | 420 | 466 | 46 | Heart | 470 | 453 | 17 |
| Maize | 330 | 346 | 16 | Liver | 670 | 751 | 81 |

crop from 0.5 cc. of the wort used in (d). The last three columns of Table I contain differences; the difference ($b-a$) gives the additional crop produced by the addition of the Bios I reagent; the difference ($c-a$) gives the additional crop produced by the addition of the Bios II reagent; and the difference ($d-e$) gives the additional crop produced by adding the extract to 0.5 cc. of wort.

1) *Effect of the Bios reagents on the crop*:—On comparing the numbers under $b-a$ with those under $c-a$, it will be noticed that while in many cases both numbers are small,¹ and other cases one is large and the other small, there is no instance where both are large. In other words, while with some extracts addition of Bios I increases the crop and with others Bios II increases it, there is no extract among those studied with which both Bios I and Bios II (added to separate portions of the extract) materially increase the yeast crop. Moreover there are no cases in which addition of either of the Bios reagents decreases the crop (giving negative values of $b-a$ or $c-a$) except such as can be ascribed to experimental error or to toxicity of the extract (see 3 below).

These findings are in harmony with the assumption that all the extracts of Table I contain a Bios I and a Bios II which are identical, physiologically at least, with those prepared from malt-combings. On this assumption, the crop obtained in Tube *b* measures the Bios II in the extract provided sufficient of the Bios I reagent had been employed; that of Tube *c* measures the Bios I; while $b-a$ gives the (physiological) excess of Bios II over Bios I in the extract, and $c-a$ that of Bios II over Bios I.

2) *Cases where neither of the Bios reagents has much effect on the crop*:—The extracts for which both $b-a$ and $c-a$ are small may be accounted for by assuming that in them the two Bioses are present in physiologically equivalent quantities; although the other possibility, that such extracts may contain a crop-increasing substance quite independent of Bios I and Bios II, is not excluded. Of all the substances of Table I, those which are least affected by the addition of either reagent are:—Wort, rice-polishings, tomato, and molasses; so these four, if any, seem the most likely to be free from Bios I and Bios II. Of the four, wort was the very first substance from which Bios I and Bios II were prepared by Lucas, and in connection with his work on pigeons he prepared them both from rice polishings; I have subjected the other two to his procedure. The results are given in Table II and show clearly that the baryta treatment separates the bios of tomato juice and that of molasses into Bios I and Bios II. Besides these four, the bios of malt-combings has been separated, indeed this substance is our standard source of Bios II; that of tea has been separated in connection with the preparation of Bios I described below; and also that of mushrooms (see p. 1107). Seven in all.

¹ The impure Bios solutions added as reagents would themselves give a Count of 30 — 50; moreover the small numbers entered under $b-a$ or $c-a$ are in most cases the differences of much larger figures, each affected by experimental error; too great stress should not be laid on the absolute values of these small differences.

TABLE II

| | |
|------------------------------------------------------------------|---------|
| a) Canned tomato juice diluted with its own volume of water. | |
| One cc. diluted juice with SS | C = 297 |
| The crude Bios I from 1 cc. juice with SS | 63 |
| The crude Bios II from 1 cc. juice with SS | 63 |
| Both together with SS | 303 |
| b) Domolco molasses, diluted to ten times its volume with water. | |
| One cc. diluted molasses, with SS | C = 300 |
| The crude Bios I from one cc., with SS | 75 |
| The crude Bios II from one cc. with SS | 62 |
| Both together with SS | 330 |

3) *Toxicity*:—The primary object of tubes *d* and *e* was to detect poisons; when the extract itself (tube *a*) gave but a small yeast crop, this result might be ascribed to lack of bios; but if (as is the case with horseradish, tobacco stems, onion juice, etc.) addition of the extract to a tube containing wort (with S & S) reduced the crop obtained from the wort alone, a poison must be present. A negative number under the heading (*b-e*), combined with a small number under (*a*) may therefore be regarded as evidence that the extract is toxic to yeast. The case of ginseng, where (*b-e*) is above zero and (*b-a*) is negative, is less certain because of the high crop obtained from the ginseng alone; this substance should, perhaps, be studied further.

4) *Effect of adding two extracts simultaneously*:—Since wort contains no great excess of either Bios I or Bios II, it might be expected that the crop obtained in tube (*d*) would not be very different from the sum of the crops obtained in tubes (*a*) and (*e*); and since sugar and salts alone give a small crop and this is counted twice in the sum, the latter might be somewhat greater. This conclusion is substantiated by the figures of Table Ia collected from the data of Table I; the greatest difference being less than 10 percent.

Additional experiments were undertaken to test the above conclusion further; the results are given in Tables III and IV. The extracts used were made up fresh, and three determinations were made with each, corresponding to tubes (*a*), (*b*) and (*c*) of p. 0000; this was obviously necessary in order to provide a basis of direct comparison with the results obtained from the mixtures. The orange, mushroom, and tomato extracts were diluted more than those of Table I, because the yeast crops recorded there are larger than are justified by critical consideration of Clark's method of analysis.

TABLE III

| | a | b | c | | a | b | c |
|-----------|-----|-----|-----|---------------|-----|-----|-----|
| Wort | 350 | 355 | 365 | | | | |
| Rice pol. | 181 | 225 | 202 | Mushroom | 157 | 305 | 121 |
| Orange | 105 | 103 | 258 | Tomato, fresh | 174 | 225 | 159 |

TABLE IV

| | Mixture | Two Crops | Diff. |
|------------------------|---------|-----------|-------|
| Wort and Mushroom | 450 | 507 | 57 |
| Rice pol. and Mushroom | 320 | 338 | 18 |
| Rice pol. and Orange | 290 | 286 | 4 |
| Tomato and Mushroom | 343 | 331 | -12 |
| Orange and Tomato | 340 | 279 | -61 |
| Orange and Mushroom | 400 | 262 | -138 |

Since mushroom contains a large excess of Bios II and tomato a small excess, while orange juice contains a large excess of Bios I, one would expect the crop from a mixture of orange and mushroom to be considerably greater than in the sum of the separate crops, and that from orange and tomato to be at least as large, while wort or rice-polishings with any of the others should give crops somewhat smaller than the sums. So far as I am aware these are the first predictions of the kind that have been made; Table IV shows that they are justified.

Looking back over this work I can see how it might be improved if it were to be repeated; for one thing, it would be advisable (using the results of Table I) to dilute the extracts which gave very large yeast crops; for another thing, stronger reagent solutions of Bios I and Bios II should be used where it is known from Table I that their addition causes a large increase in the crop, for in such cases it is quite probable that more of the reagent would have given a still larger yield of yeast; and in the third place the existence of the inactive Biogens¹ (unsuspected at the time these measurements were made), particularly that corresponding to Bios II which can easily be converted into Bios I and prepared from it again, would have to be taken into account. But even as they stand, the results discussed above seem to justify the conclusion, that not only the bios of wort, rice polishings, malt-combings, tomatoes, molasses, tea and mushrooms, but probably all the others, consist of two constituents the effect of both of which together on the yeast crop is much greater than the sum of their effects when separated.

The Isolation and Identification of Bios I

Of the materials included in Table I, tea seemed the best raw material from which to prepare Bios I; both because it contains a large excess of Bios I and because it is free from sugar which, like Bios I, is carried down by the baryta and if present would have to be removed. The first stages of the preparation were carried out by Dr. H. D. Sims and Mr. N. C. Cahoon; tannin was removed by sugar of lead, the Bios I was precipitated by lead acetate and ammonia, removed from the precipitate by carbon dioxide and water and the lead removed from this solution by hydrogen sulphide. Twenty litres of water and 4200 cc. of a 33% solution of sugar of lead were heated to boiling in

¹ Edna V. Eastcott: The Biogens. Trans. Roy. Soc. Canada, (3) 19, Sec. III, 21-22 (1925).

a copper vessel provided with a strainer and a screw press; 5 kg. of tea dust was stirred in, and boiled for 10 minutes; after which the liquid was strained off through cheesecloth and the tea pressed out. The press cake was then extracted twice more, each time with 900 cc. of the lead acetate solution diluted with 8 litres of water, and the three filtrates were united; the filtrate from a fourth extraction was mixed with water to extract the next portion of 5 kg. of tea. To the combined filtrates was added 1600 cc. of the sugar of lead solution and then 650 cc. of concentrated ammonia; the mixture was stirred for a minute and let settle half an hour; after which the precipitate (which contained the Bios I) was removed by filtration through large Büchner filters, washed, and stored under a little water. The lead precipitate from 50 kg. of tea dust was then stirred up with 10 litres of water and decomposed by carbon dioxide; this operation was carried out under a pressure of three or four atmospheres, the gas being circulated by a pump and kept bubbling through the sludge (addition of 50 cc. of coal oil prevented frothing and consequent choking of the pipes); after about 8 hours the liquid (which contained the Bios I) was removed by a press and the precipitate treated with carbon dioxide again; the combined filtrates after seven such treatments contained 86% of the Bios I present originally in the tea. The dark brown liquid so obtained was concentrated in a tinned copper vacuum pan (it did not attack the metal, a little vaseline was added to stop the frothing) and then the lead was removed by repeated treatment with hydrogen sulphide; addition to powdered charcoal (about 200 cc.) at this stage removed most of the colour and facilitated filtration. In the end it was found easiest to remove the last traces of lead by the addition of barium sulphide followed by the calculated amount of dilute sulphuric acid. The light yellow lead-free solution was then made just acid to congo paper by adding about 200 cc. of concentrated hydrochloric acid; about 200 cc. of charcoal was added, the whole was heated and filtered, and the filtrate was evaporated in vacuo in a glass vessel. When the volume was reduced to 400-500 cc. white crystals were deposited, these were filtered off, the filtrate contained the Bios I. About 250 kg. of tea dust in all was thus treated.

When two years later I began work on this solution, part had been worked up by Mr. Sims, and the rest had evidently been diluted for its volume was 8 litres; this contained 46 g. of solids (dried at 110°C.) per litre. After a number of attempts at purification by other means, I was led to the method finally adopted by observing that the efficiency of the "Bios I reagent" was not impaired by heating it with strong hydrochloric acid. After preliminary trials, 1200 cc of the black solution was precipitated by 170 g. cryst. barium hydrate dissolved in 250 cc of boiling water, the (inactive) precipitate was filtered off and the alkaline solution evaporated to half its volume in a vacuum to get rid of ammonia and volatile amines. The barium was then removed by sulphuric acid and the filtrate evaporated to 140 cc; 210 cc. conc. hydrochloric acid was added, and the acid liquid heated to 110°C in a butyl alcohol bath for 22 hours; much char was formed. The hydrochloric acid was removed by evaporation to dryness in a vacuum, the residue dissolved in water, de-

colored by charcoal, filtered, and evaporated to a volume of 35 cc. This was heated to boiling in a flask with return condenser, and 30 cc. of methyl alcohol added gradually; next morning the flask contained a large cake of crystals, which were dissolved in water and recrystallized by the use of methyl alcohol as before, they easily form supersaturated solutions in water.

Two kinds of crystals were obtained, both clear white; one of them was compact and the other leafy; on standing in the exsiccator the latter lost weight and left a fine white powder behind, while the former remained unchanged. Freezing-point determinations of aqueous solutions by Professor J. B. Ferguson gave 170-180 as the mol. wt. both of the compact crystals and of the powder; determination of the loss of weight of the leafy crystals shewed that for 180 g. of residue the loss was almost exactly 36 g., i.e. their formula contained 2 H₂O. Professor L. J. Rogers made the ultimate analysis, he found:—

| | compact cryst. | powder | C ₆ H ₁₂ O ₆ |
|----------|----------------|--------|-----------------------------------------------|
| carbon | 39.5 | 39.6 | 40.0 |
| hydrogen | 6.6 | 6.6 | 6.7 |
| oxygen | 53.9 | 53.8 | 53.3 |

The formula of pure Bios I is therefore C₆H₁₂O₆; Professor W. H. Martin found that it is optically inactive; and Professor F. B. Allan suggested that it is probably identical with inactive Inosite, also called Phaseomannite. The account of the latter given in Beilstein left no doubt that this is the case, and experiments with Kahlbaum's Inosite proved it. I wish to thank these gentlemen for their interest and assistance.

According to Beilstein¹ the inactive Inosite occurs "extremely often" in the plant and animal kingdom, he instances 35 vegetable and 11 animal products from which it has been prepared; the list he gives includes all the types of Table I. The important part played by this substance in the phenomena of growth in plants was recognized as long ago as 1856 by Vohl², who noticed that beans contain the greatest amount of "phaseomannite" when they are very young, and that with the formation of starch this substance disappears; while Meillère³ points out that inactive inosite occurs in vegetable tissues mainly during the stage of rapid growth and almost completely disappears when fruit or seeds are ripe. My own observations⁴ on the changing amounts of bios in germinating barley show, that while the inosite may have "disappeared" from the ripe grain, it is formed again when the grain begins to sprout and bios is needed for the rapid reproduction of cells in the young plant.

In view of all these observations it seemed hardly necessary to supplement the isolation of Bios I from tea by similar experiments with other

¹ Beilstein: Handb. d. organ. Chem., 6, 1194 (1923).

² H. Vohl: Phaseomannit, eine neue Zuckerart. Ann., 99, 125 (1856).

³ G. Meillère: The biochemical role of Inosite. Chem. Centralblatt, 1908, II, 1445.

⁴ Edna V. Eastcott: The Biogens, loc. cit.

sources. However, since Quercite (pentahydroxycyclohexane) is chemically so close to Inosite (hexahydroxycyclohexane), experiments were tried with it; it proved to have no influence on the yeast crop, either alone (with SS) or together with Bios II. On the whole it seems safe to conclude, provisionally at least, that there is but one Bios I, viz: Inosite; and it would be interesting to hear from other workers in this field whether their preparations contain Inosite or not, and whether such as do not contain Inosite will give a larger crop when Inosite is added—the latter are not Wildiers' "bios," but Lucas' "Bios II."

Judging from the yeast crop, the black solution made from tea (p. 1105) contains about 4 g. Inosite per litre; the hydrochloric acid treatment doubled that amount. The solution must therefore have contained, beside the inosite, some other substance which forms Inosite when hydrolysed by acid. This "other substance" is contained in tea infusion, for on treating that with hydrochloric acid (22%, 12 hours at 115°C.) its Bios I content is more than trebled; and since it remained together with the inosite throughout the long chemical treatment described on p. 0000, the two are chemically much alike. Beilstein mentions several vegetable products that would do, but here as with the Bios I isolation must precede identification.

Inosite with Bios II from Mushrooms

When direct comparison (yeast crops, using various preparations of Bios II) had shown that there is no difference between the behavior of Kahlbaum's Inosite and that from tea, I determined the counts obtained in 24 hours (see "Procedure," p. 1099; and Table V) with varying amounts of (Kahlbaum's) Inosite and of a crude Bios II solution prepared from mushrooms by mincing them, adding water, precipitating with alcohol, concentrating, adding two volumes of alcohol and precipitating with baryta (the precipitate being rejected) and removing the barium from the filtrate, in short by the method described by Lucas. Although this preparation is less effective per gram of solids it contains than Mr. Sparling's chemically treated Bios II, it was employed because there is reason to believe that his treatment fractionates the Bios II.

TABLE V

| Inosite | 1/3 | 1/6 | 1/15 | 1/30 | 1/60 | 0 | milligrams |
|---------------|-----|-----|------|------|------|----|------------|
| 2 cc. Bios II | — | — | 320 | 217 | 125 | 87 | |
| 1 cc. Bios II | 308 | 308 | 287 | 208 | 130 | 73 | |
| no Bios II | — | 25 | — | — | — | 25 | |

1) *24-hour yeast crop*:—Doubling the amount of Bios II does not much affect the crop when the amount of Inosite is small (up to 1/30 mg. in the 10 cc.); while doubling the amount of Inosite does not affect the crop when as much as 1/6 mg. is present. It may therefore be concluded that in the former case reproduction ceased because of lack of Inosite, and in the latter because of lack of Bios II. With 1/15 mg. of Inosite, doubling the Bios II begins to

affect the crop, whence it may be inferred that 2 cc. of Bios II will not be enough for $\frac{1}{6}$ mg. of Inosite, and that a third cc. of Bios II would raise the crop; this was found to be the case, the Count with $\frac{1}{6}$ mg. of Inosite and 3 cc. of Bios II is $C = 450$.

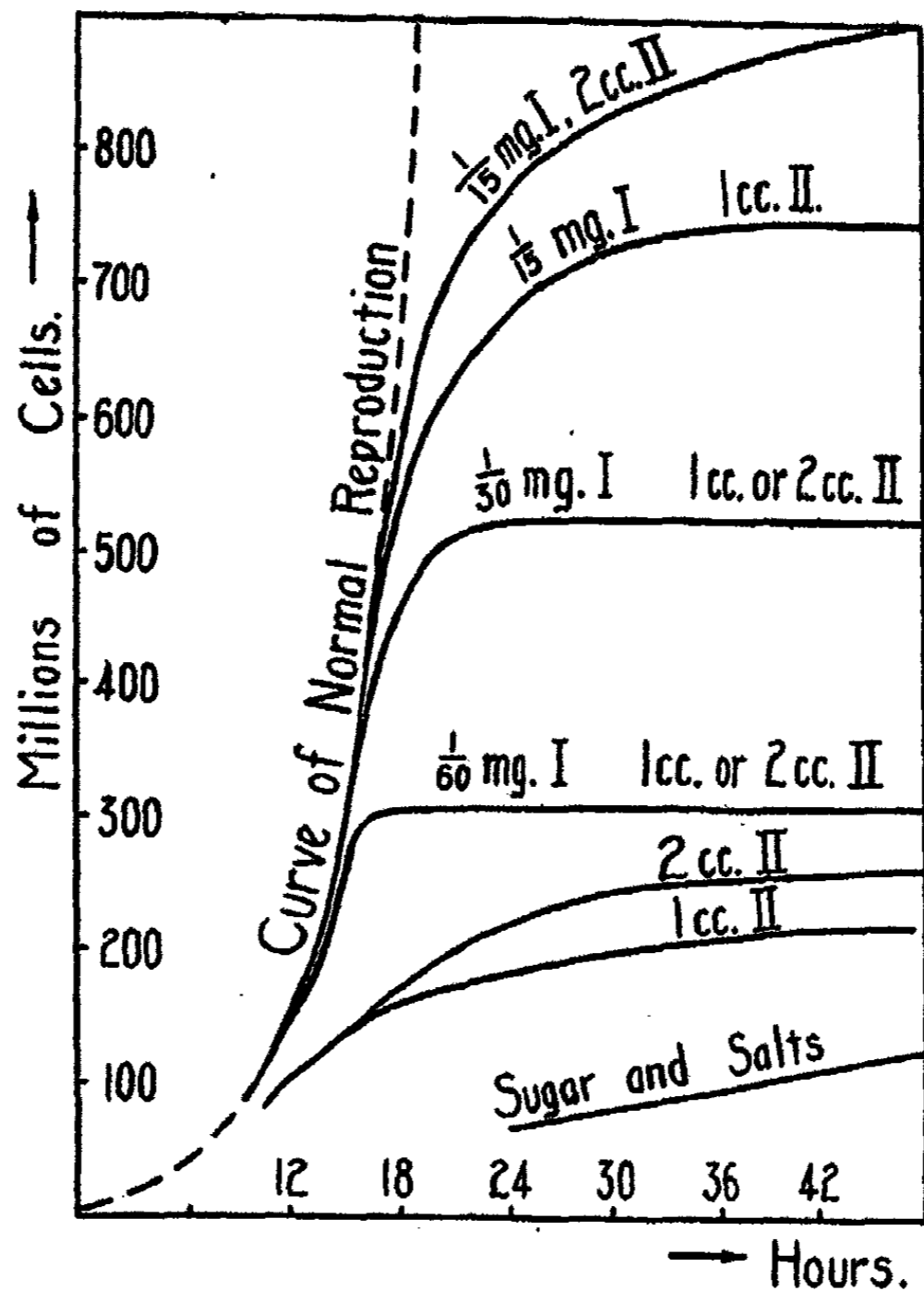


FIG. 1

2) *Rate of Reproduction*.—The 24-hour crop, although convenient for many purposes, is somewhat arbitrary; so, to link this work more closely with that of Mr. Clark, I determined the crops obtained with eight culture-media at intervals between 10 and 48 hours after seeding. The Bios I was Kahlbaum's Inosite, the Bios II was the crude mushroom preparation; large rocker-tubes were used each containing 60 cc. of the medium initially, from which portions of 2 cc. were removed from time to time to determine the Count; in all other respects the usual procedure was followed. To facilitate comparison, the yeast crops and the amounts of Bios I and Bios II employed are given in Table VI and Fig. 1., for 10 cc. of culture medium.

TABLE VI

| No Bios | | 1/30 mg I | | 1 cc Bios II | | 2 cc Bios II | |
|---------|----|-----------|-----|--------------|----|--------------|-----|
| Hrs. | C. | Hrs. | C. | Hrs. | C. | Hrs. | C. |
| 24 | 25 | 24 | 25 | 10.6 | 33 | 11 | 38 |
| 41 | 37 | 30 | 28 | 12.4 | 47 | 12.9 | 50 |
| 48 | 50 | 48 | 58 | 14.5 | 55 | 14.9 | 52 |
| 66 | 80 | | | 16.5 | 63 | 16.9 | 67 |
| 95 | 88 | 1/3 mg. I | | 18.4 | 67 | 18.8 | 73 |
| 119 | 93 | 66 | 108 | 20.6 | 70 | 21 | 83 |
| | | 95 | 130 | 23.8 | 73 | 24.2 | 87 |
| | | | | 36.1 | 83 | 36.6 | 105 |
| | | | | 41.3 | 87 | 41.7 | 103 |
| | | | | 48 | 87 | 48 | 113 |

| 1/60 mg. I 1 cc. II | | 1/60 mg. I 2 cc. II | | 1/30 mg. I 1 cc. II | | 1/30 mg. I 2 cc. II | |
|------------------------|-----|------------------------|-----|------------------------|-----|------------------------|-----|
| Hrs. | C. | Hrs. | C. | Hrs. | C. | Hrs. | C. |
| 10.6 | 43 | 11 | 47 | 10.6 | 47 | 11 | 50 |
| 12.4 | 68 | 12.9 | 75 | 12.4 | 72 | 12.9 | 83 |
| 14.5 | 100 | 14.9 | 108 | 14.5 | 117 | 14.9 | 130 |
| 16.5 | 120 | 16.9 | 122 | 16.5 | 158 | 16.9 | 167 |
| 18.4 | 130 | 18.8 | 127 | 18.4 | 180 | 18.8 | 192 |
| 20.6 | 130 | 21 | 125 | 20.6 | 197 | 21 | 208 |
| 23.8 | 130 | 24.2 | 125 | 23.8 | 208 | 24.2 | 217 |
| 36.1 | 130 | 36.6 | 125 | 36.1 | 213 | 36.6 | 233 |
| 40.8 | 130 | 41.3 | 125 | 40.8 | 213 | 41.3 | 228 |
| | | | | | | 48.4 | 227 |

| 1/15 mg. I 1 cc. II | | 1/15 mg. I 2 cc. II | | 1/15 mg. I 1 cc. II | | 1/15 mg. I 2 cc. II | |
|------------------------|-----|------------------------|-----|------------------------|-----|------------------------|-----|
| Hrs. | C. | Hrs. | C. | Hrs. | C. | Hrs. | C. |
| 10.6 | 45 | 11 | 50 | 20.6 | 253 | 21 | 290 |
| 12.4 | 70 | 12.9 | 80 | 23.8 | 287 | 24.2 | 320 |
| 14.5 | 117 | 14.9 | 130 | 36.1 | 300 | 36.6 | 348 |
| 16.5 | 170 | 16.9 | 197 | 41.3 | 291 | 41.7 | 350 |
| 18.4 | 220 | 18.8 | 253 | 48 | 291 | 48 | 365 |

Sugar and salts alone give a small crop of yeast, as Wildiers found; addition of Inosite does not increase it much; with sugar salts and the crude Bios II the crop is much the same as Lucas found with similar preparations. In media containing both Inosite and Bios II, as in Mr. Clark's experiments with wort (see p. 1095), the initial rate of reproduction is independent of the amounts of these substances the medium contains, and falls off when one of

them is exhausted. The figures show that 24 hours is not long enough to produce the maximum crop when the medium contains $1/15$ mg. of Inosite and 2 cc. of Bios II per 10 cc.; but the increase in the final yield when the second cc. of Bios II was added, confirms the conclusion drawn from Table V.

To explain the cessation of reproduction in a medium containing $1/60$ mg. of Inosite and either 1 cc. of 2 cc. of Bios II, it has been assumed above that the Inosite is exhausted 20 hours after seeding, but that the medium still contains much Bios II. To check this assumption, a tube was made up with 2 cc. of Bios II and $1/60$ mg. of Inosite in 9 cc.; after rocking 21 hours, there was added an additional $1/20$ mg. of Inosite dissolved in 1 cc. of water; thus, in all, $1/15$ mg. of Inosite had been supplied. Table VII records the yeast crops so obtained, and shows conclusively that the medium after 21 hours still contained much Bios II; enough perhaps to give, ultimately, the same yeast crop as that obtained when all the Inosite was added at the beginning; the form of the crop-time curve is most suggestive, but the experimental work to which it has given rise is not yet ready for publication.

TABLE VII

| | | | | | | | | | |
|-------|-----|------|------|------|------|------|------|------|-----|
| Hours | 21 | 22.9 | 24.7 | 26.7 | 28.8 | 32.7 | 34.8 | 45.2 | 48 |
| Count | 120 | 120 | 125 | 128 | 138 | 167 | 188 | 200 | 275 |

Recovery of Inosite from the Yeast Crop

The circumstance that Inosite is not affected by heating with concentrated hydrochloric acid, suggested a comparison between (a) the amount of Inosite taken out of the culture medium during the reproduction of the yeast and (b) the amount of Inosite that can be obtained by hydrolysing the yeast crop. Two milligrams of Inosite, excess of a highly concentrated Bios II from malt-combings, and 150 cc. of the S & S were seeded as usual in a total volume of 300 cc. (6 large rocker-tubes); after 24 hours the Count was determined ($C = 230$) and the yeast was filtered off; the filtrate contained no Inosite, and some Bios II. The total crop ($300 \times 230 \times 250,000 = 173 \times 10^8$ cells), after washing on the filter, was heated (paper and all) with 45 cc. of 22-percent hydrochloric acid to 110°C .; after which the acid was removed by evaporation to dryness in a vacuum, and the residue dissolved in water and made up to 61 cc. One cc. of this solution with sugar, salts and Bios II (see "procedure" p. 0000) gave a Count of $C = 202$. In order to interpret this result, the crop obtained from the same amount of the same Bios II with varying amounts of Inosite were determined; they were:—

TABLE VIII

| | | | | | | |
|---------|---------|---------|--------|--------|--------|------------|
| Inosite | $1/240$ | $1/120$ | $1/60$ | $1/40$ | $1/30$ | milligrams |
| Count | 73 | 105 | 148 | 173 | 197 | |

Thus the amount of Inosite obtained by hydrolysis of the yeast crop was $61 \times 1/30 = 2.03$ mg., whereas 2.0 mg. had been consumed during the growth

of the crop. The Inosite used up was quantitatively recovered. Thus each cell of "normal yeast" took up and yielded again 1.2×10^{-13} g Inosite, which is about 1 or 2 parts per thousand of its own dry weight.

In view of this result it seemed of interest to ascertain whether Inosite can be obtained by the hydrolysis of yeast grown with sugar and salts alone; i.e. whether the yeast plant can slowly synthesize whatever it is that Inosite in the medium supplies, or has a chemical composition depending on the medium in which it was grown. With this object, 25 cc of SS, 20 cc of water, and 5 cc of yeast suspension were pipetted into each of five large rocker-tubes; the seeding was to a Count of 1.5, i.e. $450 \times 1.5 \times 250,000 = 1.7 \times 10^8$ yeast cells were used as seed. After 5 days rocking at 25°C., the Count was $C = 92$, i.e. the crop was 103×10^8 cells. These were filtered off and hydrolysed as before; they yielded 0.5 mg of Inosite, i.e. 0.5×10^{-13} g. per cell, about half as much as the normal yeast.

Summary

The crops of yeast obtained under standard conditions from 48 vegetable and 15 animal preparations have been determined; also the crops when either Bios I or Bios II or wort was added to the extracts.

From these results it is possible to predict, roughly, the crops obtainable from mixtures of two extracts; on the assumption that in every case the bios in these extracts consists of Bios I and Bios II.

The bios from seven sources has been fractionated by Lucas' method into Bios I and Bios II.

Bios I has been isolated from tea dust; it proves to be identical with inactive Inosite.

Curves showing the rate of reproduction of yeast in solutions containing salts, sugar, Inosite and crude Bios II, agree in form with those obtained by N. A. Clark with solutions of salts, sugar and wort.

The Inosite taken up by yeast from the culture medium can be quantitatively recovered by hydrolysing the yeast crop; each normal cell takes up, and yields, 1.2×10^{-13} grams of Inosite, i.e., 1-2 parts per thousand of its own dry weight.

Yeast grown in a solution containing only sugar and salts, also yields Inosite on hydrolysis, but in less amount.

I am glad to express my acknowledgments to Professor W. Lash Miller, under whose direction this investigation has been carried out.

*The University of Toronto,
Chemical Laboratory
May 1928.*

NEW BOOKS

The Properties of Silica. By Robert B. Sosman. 23 X 16 cm: pp. 366. New York: Chemical Catalog Company, 1937. Price: \$12.50. On p. 18 the author gives his own summary. "The chemist's task comes first. Having discovered a substance called silica, which can be caused to disappear by various means, then to reappear with its original properties, he proceeds to dissect it into its more elementary constituent substances silicon and oxygen, distinguishing also between three kinds of silicon which he finds in it. (Chapter II.)

"Going still deeper into its mass composition he examines the constitution of the atoms and the little that is known about the mode in which they combine to form the substance silica (Chapter III.)

"His knowledge of atoms and their modes of arrangement and combination being too scanty to permit of further logical progress in this direction, he starts on a new tack, and collects all the different kinds of pure silica that can be found or made. Some of them, it turns out, differ in properties from others, and behave differently when heated or stressed. They are the *polymorphous forms and states of aggregation* of silica. The complete description of their relationships as affected by temperature and pressure can be embodied in a *phase-rule diagram* (Chapters IV, VI, VII, VIII), and their *rates of transformation* may be studied empirically at the same time (Chapters V, VII.) The practical necessity of treating the micro-phases separately is also recognized. (Chapters IX, X, and XI.)

"One obvious consequence of the atomic constitution of silica is the existence of differences in *symmetry* and in certain characteristic *dimensions* between the polymorphous forms. (Chapters XII and XIII.) To round out the picture, *hypotheses* of structure and polymorphism must now be brought in (Chapters XIV to XVII.)

"The chemist is now ready to examine and record the fundamental properties of his collection of polymorphous forms, those properties which will enable him to predict completely the behavior of silica under any conceivable circumstances. He recognizes at once a relation between the fundamentals *M* and *L*, namely, that the ratio of *M* and *L* is a quantity characteristic of each form of the substance,—its *density or specific volume*. (Chapter XVIII.)

"By this time the physicist has had to be called in to explain what controls the appearance and disappearance of the forms discovered in the earlier chapters. The cause sought for proves to be a relation between the fundamentals *U* and *S*,—energy and entropy,—most conveniently stated in the form of a property called the *zeta*, whose study requires the measurement of the *heat capacities* and *latent heats* of the forms. (Chapter XIX.)"

"The reader whose training has been in chemistry or ceramics rather than in physics will perhaps be disappointed in not having found in this or in succeeding chapters any reference to the 'chemical properties of silica.' But it will be seen easily that from the point of view adopted for this presentation there is no such thing as a chemical property of an individual substance, unless we wish to include under that term the conditions of equilibrium and the rates of transformation of its polymorphous forms. Chemistry is concerned with the interactions between two or more substances, and chemical properties may only be spoken of, consequently, in connection with a system of two or more components. The solubility of silica in water, for example, is not a property of silica, but an item in the general plan of the two-component system $\text{SiO}_2\text{:H}_2\text{O}$," p. 20.

"The eight better-known modifications and their temperature-ranges of stability are as follows: low-quartz, stable at atmospheric temperatures and up to 573°C; high quartz, stable from 573°-870°—capable of existence above 870° but is then not the stable form; low-tridymite, capable of existence at atmospheric temperatures and up to 117°, but is not the stable form in this range; lower high-tridymite, capable of existence between 117° and

163°, but is not the stable form in this range; upper high-tridymite, capable of existence above 163° and is the stable form from 870° to 1470°—above 1470° it is again unstable—melts at 1670°; low-cristobalite, capable of existence at atmospheric temperatures and up to 200°-275°, but is not the stable form in this range; high cristobalite, capable of existence above 200°-275°, and is stable from 1470° to 1710°, its melting point; vitreous silica or silica glass, capable of existence at atmospheric temperatures and up to 1000° or above, where it begins to crystallize with measurable rapidity, but is an unstable, under-cooled liquid (a *glass*) at all temperatures below 1710°", p. 41.

Since vitreosil is pre-empted, the reviewer suggests condensing vitreous silica into vitail, p. 44.

The author differentiates, p. 47, between two types of inversion in silica: (A) the *sluggish* type, and (B) the 'prompt-reversible' or *high-low* type. To the sluggish type belong the inversion of quartz to tridymite at 870°, the inversion of tridymite to cristobalite at 1470°, and the melting of cristobalite at 1710°. To the high-low type belong the inversions sometimes called the 'alpha-beta' inversions, low-quartz to high-quartz at 573°, low-tridymite to lower high-tridymite at 117°; lower-high tridymite to upper high-tridymite at 163°; and the low-cristobalite to high-cristobalite at 200° to 275°."

For the ready and sure conversion of quartz into tridymite the presence of some other substance or substances is necessary. The effect of the added substances seems to be principally the forming of a liquid melt or flux whose presence greatly accelerates any changes and may lead directly to the formation of the stable phase," p. 62.

"Although there is no question that silica is appreciably volatile at a white heat, not all of the observed vaporization of silica is a true evaporation of the compound SiO₂. In addition to its true evaporation there is under certain conditions an apparent evaporation which is not due to vaporization at all but to reduction and reoxidation. In a reducing atmosphere, such as exists in a carbon-tube electric furnace, abundant white vapors of silica are frequently seen, which result from (1) the reduction of SiO₂ to Si, (2) volatilization of the silicon, which is much more volatile than silica, and (3) reoxidation of the Si to SiO₂ either through admixture with air or through recombination with the original oxygen in a cooler part of the furnace," p. 107.

"The form of the time-temperature curves observed by Bates and Phelps deserves special remark. The temperature of a thermocouple inserted in the quartz plate is plotted against time, with the temperature of the furnace rising steadily but very slowly, and that of the plate rising with it. At a certain instant, coincident—where the two are both being read—with the moment when the readings of rotatory power are brought to an end by the beginning of the inversion, the temperature begins sharply to depart from its previous smooth course. After a few minutes it gradually returns to its original rate of increase. The departure thus represents an absorption of heat due to the inversion.

"The interesting feature is that the temperature of the couple actually *falls* after the inversion has begun. Now it is a well-established principle that when two phases of a substance are in thermodynamic equilibrium at a fixed pressure, the temperature is absolutely constant. When a metal or a salt is heated, the temperature of a thermocouple immersed in the material rises to the melting point and remains there while melting is going on. A drop in its temperature after melting has begun means simply that it has been accidentally and temporarily heated hotter than the substance, and the true melting point is not the point where the temperature begins to depart from a smoothly rising curve, but the point to which it drops while melting is in progress.

"By analogy with a melting point, the inversion point of the quartz plate would be expected to be some constant temperature toward which all the curves would fall. But the constant point in Bates' set of curves is not the minimum, but the *beginning*, which reproduces itself within $\pm 0.1^\circ$, while the minimum varies with the rate of heating or other conditions. It reproduces itself not only when the thermocouple is inside of the crystal but even when the couple is only lying upon the surface.

"Is there any other explanation for the drop in temperature, consistent with looking upon the inversion as analogous to a melting? One possibility is that when the inversion

begins there is a sudden change in the relation between axial and equatorial conductivity, such that the thermocouple can be rapidly cooled by a colder part of the plate; this could be tested experimentally. Or, since quartz is very transparent to long wave-lengths beyond its adsorption bands (see XXXVI), the couple may be superheated by radiant heat from the furnace, and be then pulled back by the inversion.

"If we reject these explanations as unlikely, then we must admit that the inversion is not like melting, proceeding gradually from level to level as the necessary heat is supplied, but that it spreads almost instantly through the whole crystal when once it has started, with the result that the parts which are not yet supplied with sufficient latent heat to cause the inversion to proceed directly are compelled to draw upon their heat capacity and so to become colder. This is the view that seems to be forced upon us not only by the facts brought out in Bates and Phelps' investigation but also by other phenomena mentioned in this and other chapters, but before adopting so radical a view we should have further experimental evidence.

"The foregoing remarks apply also to the reverse change on cooling, except that the temperature of beginning varies within a range of 0.6° instead of 0.2° . Heat is released and the temperature of the thermocouple rises, *toward* the equilibrium-temperature if we consider melting as the true analogy, *above* the equilibrium if we consider that it is a case of forced inversion.

"It is still possible to bring the idea of a forced inversion into line with the general principles already stated. It is known that stress lowers the equilibrium-temperature in such cases as melting and solution. It may be expected also to lower the inversion-temperature. When the inversion begins on the outside of the fragment the change of volume and of axial ratio in the outer portion throws the rest of the plate into a state of stress which is sometimes great enough to cause fracture. We need only suppose that this stress may so lower the inversion-temperature of the uninverted portion that its stored heat is enough to produce the inversion. A lowering of several degrees would be required, however," p. 122.

"Lawson has recently recorded an observation made a number of years ago, which is of interest in connection with this subject. It is known that crystalline quartz is colored yellow-brown or brown-red by the radiation from radioactive substances, sometimes in streaks. Vitreous silica is usually colored a uniform brown-violet by similar radiations. Lawson recalls the occurrence of spiral streaks of dark violet in a vitreous silica dish used by Hönigschmidt in 1911 for the recrystallization of radium chloride. No color appeared between these streaks, which extended almost to the rim. When the glass was heated in a Bunsen flame the color disappeared with the production of a brilliant blue-violet luminescence.

"This decided difference in coloring under the action of radium indicates a difference in constitution between the colored and colorless streaks of the dish, which may be of the same character as the crystalline and non-crystalline ribbons in the glass examined by Rayleigh," p. 141.

"Most of the theories of structure of silica agree in giving to the triplet SiO_2 a triangular plan. As McKeehan points out, this may have an effect on its state of aggregation at a given temperature. The analogous compound carbon dioxide takes the form of gaseous molecules of CO_2 , each of which is symmetrical about an axis passing through all three atom-centers. It may therefore be expected to have relatively weak stray fields outside the molecule, and hence the mutual intermolecular attractions which cause condensation to the liquid form are small. A similar high degree of molecular symmetry in silicane, SiH_4 , gives to this compound, as to CO_2 , the ability to become a gas at a relatively low temperature," p. 242.

"At the same time we must not lose sight of one essential quality of a genuine hypothesis. It must not explain the phenomena with too much facility. It is no real virtue in a theory of polymorphism, for instance, that it is capable of explaining not only all the existing data but also any imaginable facts of polymorphism which remain undiscovered. A theory which is capable of explaining all imaginable data in its field is, conversely, incapable of predicting any one experimental fact to the exclusion of any other; or, in the pragmatic philo-

sophy, it is not a theory at all, but a form of words. It has happened more than once in the history of science that two formulas which sounded very different, but whose corollaries were experimentally indistinguishable, have led to needlessly long and bitter polemics. Hence it will be well to devote our closest scrutiny to the deductions that follow from a given hypothesis, rather than to the plausibility and general attractiveness of the formulation itself," p. 244.

The author makes the following postulates in regard to silica, pp. 245-260:—

(A) Silica exists as an individual triplet in all of its states of aggregation—gaseous, liquid, vitreous, and crystalline.

(B) The solid state in silica is the result of a sharing or a transfer of electrons between neighboring atom-triplets.

(C) The sluggish type of inversion in silica depends upon a fundamental rearrangement of silicon and oxygen atoms.

(D) The high-low type of inversion in silica goes deeper into the atom than the sluggish type, but involves also a subordinate change in the relative position of the atoms.

(E) The fundamental building unit of silica is a silica thread built up of SiO_2 atom-triplets.

(F) The electrons of the outer octet about each atomic nucleus are associated in pairs.

(G) The solid state in silica is partly due to the interlocking of electron orbits of oxygen and silicon atoms in the neighboring silica threads.

(H) Every piece of glass, as originally drawn, cast, or blown, has a structure of its own just as a tree, sea-shell, or concretion has its own structure; this structure is the resultant of its *mechanical* history.

(I) Superposed on the mechanical structure is a finer structure which is the resultant of the *thermal* history of the glass, and which can therefore be changed and brought to a fairly reproducible state by the thermal annealing, but without greatly altering the original mechanical structure.

(K) The mechanism of the high-low inversions is similar in all the forms of silica.

(L) The high-low inversions in silica consist (with rising temperature) (a) in an increase of amplitude of the thermal vibration of a pair of atoms which (b) influences the manner of revolution of a pair of electrons, with the result that (c) a relatively constant attraction between the two atoms becomes balanced by an increasing repulsion between the two orbits in question.

(M) The structure of cristobalite is incomplete; part of the oxygen atoms are in undefined or haphazard positions.

(N) The proportion of haphazard oxygen atoms in cristobalite increases with the temperature, and is preserved by rapid cooling to temperatures of 300° or lower.

(O) The structure of high-cristobalite is heterogeneous on a sub-microscopic scale.

The author considers that "chalcedony is a submicroscopic mixture of fibers of quartz with interstitial amorphous silica; a variable amount of water is also held among the fibers, but is not essential to the mineral," p. 272.

"There are in the published records many data on the habit of natural quartz in association with rocks which are assumed to have been above 573° when the quartz crystallized, and these observations might be supposed useful as a basis for selecting the forms characteristic of high-quartz. But the reasons for the assumed temperature are usually not very strong, and the line of argument, furthermore, has no logical validity unless the observer has seen the quartz crystallizing and knows by measurements of temperature that the magma was above 573° at the time. It might seem unnecessary to insist upon this point, were it not for the fact that the petrologists have been trying in recent years to use quartz as a 'geologic thermometer' and to deduce its temperature of formation from its observed properties. Now it is obviously bad science to proceed by first assuming a temperature and then using the properties deduced therefrom to prove that the temperature had the value assumed. The only safe course is to set aside for later use all the petrologic data on the habit of quartz, and hold strictly to the experimental data," p. 501.

"The luster of quartz is usually described as 'glassy,' which means that its surfaces are usually optically smooth and reflect the visible portion of the spectrum without any noticeable selective absorption. The luster, especially of the conchoidal surfaces of fracture, is sometimes described as greasy? Undoubtedly there is a difference between 'greasy' and 'glassy,' the former involving perhaps a recognition of scarcely visible undulations on the surface," p. 716.

"The best present evidence indicates that the color of most specimens of amethystine quartz is due to a compound of iron; that of most of the rose quartz, to a compound of manganese; and that of most of the smoky quartz, to silicon set free by the radiations from radioactive elements. There are other causes of color, but they appear to be less important than the causes mentioned. In most instances the colors are irreversibly destroyed by heat," p. 798.

"If the cloudiness or color is due entirely to the scattering of light by small particles, then smoky or yellow quartzes should be just as transparent to the ultra-red as visually clear quartz, because the scattering is effective in inverse proportion to the fourth power of the wave-length: $\lambda^4 \log (J_0/J) = \text{constant}$. Doubling the wave-length, say from deep red at 0.8μ to near ultra-red at 1.6μ , would thus reduce the scattering to one-sixteenth.

"A specimen examined by Raman was in fact found transparent to ultra-red. Koenigsberger measured the transparency of brown smoky quartz at many points between wave-lengths 0.8 and 4.0μ , and found the curve from 1.2 to 4μ to be identical with that for transparent quartz, differing from it only in the region near the visible spectrum," p. 799.

Wilder D. Bancroft

Thermionic Phenomena. By Eugene Bloch. Translated by J. R. Clarke. 19×13 cm; pp. x + 145. New York: E. P. Dutton and Company. Price: \$2.50. The chapters are entitled: introduction; historical; experimental arrangements; the electronic emission in a vacuum (2); the distribution of velocities and the exchanges of energy in electronic emission; the saturation curves in pure electronic emission; the effect of gases on the electronic emission; the emission of positive ions by metals in a vacuum and in gases; the emission of ions by heated salts; the application of thermionic phenomena to the measurement of high vacua and to the rectification of alternating currents.

"Let us mention the sole exception to the validity of Richardson's formula which has been discovered up to the present. This exception, announced by Richardson and Cooke, is in the case of osmium: the straight lines of the preceding graph are replaced by a broken line made up of two straight lines inclined to each other at a definite angle. It is probable that two allotropic modifications of osmium exist, each of which has its characteristic emission, there being a transformation point at a certain temperature," p. 31.

"It should be mentioned that Arnold has sometimes accidentally observed emissions which are very much stronger than those normally yielded by the mixtures of oxides of the alkaline earths. Perhaps these emissions may be due to fortuitous mixtures of impurities with the normal oxides. This should lead to the systematic examination of mixtures of refractory materials; it is not impossible that this might result in the discovery of substances which are still more active than those at present in use," p. 40.

"If a fixed potential difference of say 100 volts is applied between a tungsten cathode raised to a high temperature and a cold anode, and the curve constructed which represents the current received as a function of the temperature, it might be expected that the classical curve of Richardson would be obtained, and this actually would be the case if saturation were always realized. Experiment shows that in reality the current, after having commenced to increase in accordance with Richardson's law, ends by departing from this law, assuming values less than the theoretical values and at high temperatures becoming *rigorously constant*," p. 56.

"The explanation of the Langmuir curves must be sought in the mutual repulsion of the electrons emitted by the filament. This repulsion, which is negligible when the number of electrons is so small that the current does not exceed a small fraction of a milliamper, becomes, on the contrary, very considerable when the temperature of the filament is high

enough for the electronic current to be greater than a milliampere. In this negative case there exists in the space between the electrodes a negative charge, the density of which is very appreciable. The field of mutual repulsion which results therefrom is superposed on the accelerating field so that saturation becomes more difficult. As the temperature of the filament is increased, there comes a time when the space charge is such that the field it produces sends back to the cathode all the electrons which leave it; after this the current shows no further increase, whatever the temperature of the filament," p. 57.

"If a tungsten filament is heated momentarily in a well-evacuated tube to a temperature of 3,000 degrees absolute it partially volatilizes and forms a black deposit of metallic tungsten on the walls of the tube. If a trace of chlorine is now introduced into the tube in the cold it does not appreciably attack either the filament or the deposit, even though the tube be heated to 200 degrees. But if the filament be raised to a bright red heat, keeping the tube cold, the deposit of tungsten *on the tube* is seen to disappear rapidly without the heated filament suffering any visible alteration. It is probable that the molecules of chlorine have been dissociated into active atoms by their collisions with the heated filament and that the atoms thus produced, projected in straight lines toward the walls without being able to recombine *en route* with other similar atoms, unite there with the tungsten at ordinary temperature.

"The experiment is still more striking when two filaments which can be heated independently are placed in the same evacuated tube. If a trace of chlorine, which has no action on tungsten in the cold, be again introduced and one filament is heated, it is found that it is only the *other* filament, kept at the ordinary temperature, which disappears gradually under the action of the chlorine," p. 88.

"It has been seen that in kenotrons as at present made the alternating voltages brought into action are always high, and are reckoned in thousands or in tens of thousands of volts. It would appear at first sight that there would be little danger with these voltages from the point of view of their electrostatic actions, since in the normal working of the kenotron the voltage across the terminals of the most powerful kenotrons does not exceed a few hundred volts. It should not be forgotten, however, that this working is intermittent, and that in every alternation the current only flows during half the period. It is during this half period, which can be called the useful half period, that the foregoing arguments are applicable, and that the voltage across the terminals falls to a few hundred volts. During the other half period, which can be called the half period of rest, the current falls to zero. At this instant no power is expended in the apparatus but, on the other hand, it behaves as an infinite resistance, which means that all the voltage of the source is thrown across its terminals. Thus during every period of the alternating current the voltage across the terminals of the kenotron passes regularly from a value of the order of a few hundred volts to a value of the order of tens of thousands of volts. As the electrostatic action which two conductors exert on each other varies proportionally to the square of the difference of potential between them, it follows that the mechanical forces exerted on the filament during the half period of rest are not at all negligible. If the filament is too fine or insufficiently supported it will commence to vibrate with a frequency equal to that of the current which is being rectified, and a rapid deterioration, or even a rupture of the filament may result. For this reason designers have been led to search for methods of construction as robust as possible, especially in the case of kenotrons to be used at high voltages," p. 131.

Wilder D. Bancroft

Laboratory Manual of Colloid Chemistry. By Harry N. Holmes. Second edition. 23 x 15 cm; pp. xviii + 228. New York: John Wiley and Sons, 1928. Price \$3.00. This volume is double the size of the first edition and is also much better. "Much new material has been added on Sedimentation in Chapter I, on Electrodialysis and Ultrafiltration in Chapter II, on Surface Tension in Chapter VIII, on Gels in Chapter IX, on Viscosity and Plasticity in Chapter XV, and on Soils in Chapter XIX. Adsorption, the heart of the subject, has gained greatly in the numerous new experiments, while entire new chapters have been added on Froths and Films, The Colloid Chemistry of the Proteins, and Aerosols."

Among the interesting things are Kahlenberg's experiments on dialysis through cholesterol membranes, p. 23; the color of photographic images, p. 61; the compression of water by hydration, p. 110.

The theory of rhythmic banding, p. 145, harks back to the erroneous view of supersaturation. The account of Saylor's work on crystallisation, p. 161, is pretty bad. Fall's work on washing is included, p. 117, and there is a comparison, on p. 195, between Patrick's and Holmes' silica gels which will not please Patrick.

Wilder D. Bancroft

The Chemistry of Leather Manufacture. Vol. I. By John Arthur Wilson. *Second edition.* 23 × 16 cm; pp. 496. New York: Chemical Catalog Company, 1928. Price: \$10.00. The first edition has been translated into German, French, and Russian. There is so much new material to be added that the second edition is in two volumes of which this is the first. The arrangement of the subject is such that we don't get to tanning in this volume, the last chapter dealing with the chemistry of the tannins.

There is quite an increase in the number of the superb photo-micrographs. The most marked change is in the classification of the tannins, p. 458. The division into pyrogallol tannins and catechol tannins is apparently obsolete, p. 458. "Perkins divides the tannins into three groups: the α group contains the depsides or gallotannins; the β group the diphenyl methyls or ellagitannins; and the γ group the phlobatannins, or catecholtannins." Freudenberg divides the tannins into two main categories, each with three subgroups: hydrolyzable tannins in which the benzene nucleus is united to a large complex through the oxygen atoms; condensed tannins in which carbon linkages hold the nuclei together.

On the theoretical side the author is still weak. He believes that there is a definite relation between pH and hydrogen ion concentration, p. 103, and, the effect of salt is due to hydration, p. 124. The paragraph still stands, p. 141, in regard to the action of hydrochloric acid on gelatine, that "the agreement between calculated and observed values is absolute within the limits of experimental error. For this reason Procter and Wilson regard their theory as proved, but, if further corroboration is desired, it can be found in the extensive researches of Loeb, some of which will be described later. *It is worthy of note that no theory of swelling has yet passed the stage of qualitative speculation.*"

As a concession to facts, the author does mention, p. 178, that one can consider hydrochloric acid as adsorbed by gelatin; but nobody would guess from the text that this gives the same equation.

Wilson tries to save Loeb's face in regard to the Hofmeister series, p. 145. "This was not, as many later writers seem to have supposed, a claim that the Hofmeister series is not apparent in any protein reactions, but merely proof that this series is not apparent in those phenomena which are determined entirely by the Principles of the Donnan equilibrium. Loeb has been much misquoted and criticized for claims he did not make."

Whatever mistakes Loeb may or may not have made, he was a good fighter and did not pussyfoot. When he said that the Hofmeister series was a myth, he meant just that. He would not have been grateful for this sort of defence.

There is a curious paragraph on p. 238. "The theory [of Gustavson] also suggests an explanation of the fact that a mixture of calcium chloride and sodium chloride is less destructive of skin protein than either salt used alone. These salts may form addition compounds with each other that are more stable than the addition compounds that they would otherwise form with the protein. The tendency for the salts to combine with protein, causing destruction, is thus materially reduced. A parallel case is that of the elements sodium and chlorine, which are highly reactive in certain respects when taken alone, but very much less active in the compound sodium chloride."

Wilder D. Bancroft

Anorganische Chemie. By Robert Schwarz. 22 × 15 cm; pp. xi+139. Dresden and Leipzig: Theodor Steinkopff, 1927. Price: 8 marks; bound, 9 marks. In the preface the author says that he has confined himself to experimental inorganic chemistry, so as not to

interfere with the fields of physical chemistry, etc. There is a preliminary general part and the special part is presented under the headings of non-metals, metals, and complex salts.

There are a number of interesting facts in the book. The blue color of Prussian blue is attributed to the presence in the same molecule of bivalent and trivalent iron, p. 8, though the author does not draw the corollary that magnetite is or should be blue. Nitrogen sulphide occurs in a red form which can be converted irreversibly into a blue form, 29. Fichter has obtained a good yield of persulphate by the action of fluorine on a potassium persulphate solution, p. 32; but the author is wrong in saying that this accounts for the addition of fluorides in electrolytic oxidations. The perphosphate, $K_4P_6O_{20}$, has been made by electrolytic oxidation of dipotassium phosphate in presence of fluorine ions, p. 55.

"The monomeric molecule, SiO_2 , corresponding to carbon monoxide, has not yet been prepared; but may perhaps exist in the vapor given off above 2000° The molecular size of the liquid silica has been fixed at $(SiO_2)_n$ by determination of the lowering of the freezing-point of lithium metasilicate on addition of silica," p. 64. The author believes that he has proved the existence of the definite chemical compounds, H_2SiO_2 , $H_4Si_2O_6$, $H_6Si_3O_9$, and $H_8Si_4O_{12}$, p. 67.

Anschütz and Riepenkröger claim that orthoboric acid decomposes in presence of hot steam into water and volatile HBO, which recombines with water on cooling, p. 78. When lithium hydride is electrolyzed, lithium is given off at the cathode and hydrogen at the anode, thereby indicating the existence of a hydrogen anion, p. 81. This agrees with the crystal lattice of the lithium hydride, in which the lithium occupies the same position as the sodium in sodium chloride crystals.

Scagliarini and Torelli have prepared the oxide Cu_2O_3 by oxidation with sodium peroxide in alkaline solution. This may react with alkali and give the instable, red cuprate, which probably has the formula $KCu(OH)_4$, p. 84. Tungsten has been obtained by the electrolysis of fused alkali tungstates, p. 109. It seems probable that tungsten belongs in the electrochemical series between zinc and iron.

"Schwarz has observed a remarkable change in the catalytic decomposition of hydrogen peroxide when the latter is exposed to x-rays, the platinum being poisoned by these rays but recovering slowly from the effects," p. 118. The assumption is made that this is due to the decomposition of water and to the poisoning of the platinum by active oxygen. When platinized asbestos is exposed to x-rays in the absence of water, there is a distinct increase in the rate at which sulphur dioxide is oxidized.

Wilder D. Bancroft

Lehrbuch der physikalischen Chemie. Vol. I. By Karl Jellinek. Second edition. 25 x 17 cm; pp. liii+988. Stuttgart: Ferdinand Enke, 1928. Price: paper, 82 marks; bound, 86 marks. This book is intended frankly to form a bridge between physics and chemistry. That means five volumes and, as a preparation for it, the author spent three years studying non-euclidean geometry, vector analysis, astronomy, physics, etc., as a preparation for relativity theory. This volume deals with pure liquids and gases.

The author takes D. Berthelot's figure of 22.412 liters for the gram molecular volume of oxygen at 0° and one atmosphere pressure, p. 28. With the centigrade zero at 273.09 Abs., this makes $R = 0.0821$ liter atmospheres per degree. Since $C_v = 3R/2 = 2.978$ cal., $C_p = 4.963$ cal., and $C_p/C_v = 1.666$, p. 198. With dilute gases the collisions with the walls of the containing vessel play an important part, p. 263. It is not justifiable to treat these collisions as completely elastic ones. Knudsen has found that the amount of carbon dioxide going through a capillary at low pressure is fifty thousand times as much as one would calculate from the simple Poiseuille Equation, p. 277.

The author ascribes the abnormal behavior of water in regard to density and fluidity to polymerization, though he does not go into details. The less polymerized form of water is less viscous than the more polymerized form, contrary to the assumption that has been made that the increase in the number of molecules necessarily increases the viscosity, pp. 434, 442, 449, 452, 490, 492, 498.

Young's test of the reduced equation of state is given on p. 704 and Nernst's on p. 706 while data from the theorem of the rectilinear diameter are on p. 709. There is an excellent discussion of the corrections to the van der Waals equation, beginning on p. 720. The equations of state of D. Berthelot, of Wohl, and of Dieterici are discussed at considerable length; but Keyes gets barely more than one line, p. 794.

The author presents the phenomena primarily from the point of view of Laplace, p. 834, according to which there is a surface of discontinuity between liquid and vapor. According to van der Waals and to Bakker, there is a continuous gradient between them, p. 859. Bakker considered this film to be about five molecular diameters at $T_r = 0.9$ and four hundred molecular diameters when $T_r = 0.999$.

The author points out, p. 889, that one can not draw definite conclusions about molecular association of liquids from Trouton's law; but he does not make it as clear as he should why this is not legitimate. From Cederberg's formula, p. 890, water and helium are only a little more out of line than oxygen and methyl acetate.

Wilder D. Bancroft

Photochimie. By A. Berthoud. 21 × 14 cm; pp. viii + 323. Paris: G. Doin et Cie., 1928. Price: 40 francs. There is a real dearth of books, good, bad or indifferent, on Photochemistry. For many years the most valuable was the short monograph by Weigert, published in 1911 in the Ahrens Collection (*Die chemischen Wirkungen des Lichts*) but, unfortunately, never brought up to date. This gap in our physico-chemical literature has now been, in a large measure, filled by the present volume, written by one who has himself contributed materially to the advance of his subject. Professor Berthoud explains his point of view in his preface. He does not set out to write a comprehensive treatise on the subject. Rather, he concentrates on such quantitative laws (or rules, as he prefers to call them) which have emerged during the last few years from the now large mass of available experimental data, and selects from the latter such examples as will serve to illustrate the former. He is particularly careful to emphasize the fact that many of these data depend on experiments carried out under conditions now recognised to have been insufficiently controlled, and that an element of doubt consequently attaches to the deductions made from them. Experimental work in photochemistry is indeed characterised by the large number of factors which must be quantitatively specified if significant results are to be obtained, and, in its present state of development, it is necessary to scrutinize closely even the results of workers of recognized skill, before accepting them. Professor Berthoud recognizes this and, whilst being interesting throughout, never becomes dogmatic. The book falls into two parts. Part I forms a 50-page introduction to Part II, and contains a résumé of both facts and theories concerning those physical aspects of light emission and of the transportation of radiant energy which are of primary importance to the photo-chemist. It is clearly and concisely written.

Part II deals with photochemistry proper. It commences with a short chapter on chemical kinetics, including the concept of critical energy. The Grotthuss-Draper Law is then discussed in its various aspects, culminating in the Einstein-Stark photochemical equivalent conception. The great impulse given to the subject by the enunciation of the latter is clearly seen on reading this chapter. The author then deals at length with photochemical kinetics, including his own important researches, and introduces the subject of reaction mechanism. Photochemical Catalysis and Optical Sensitisation are next treated, whilst the last eighty pages are chiefly devoted to phototropy, chlorophyll assimilations and photopaphy. Interesting in themselves, they detract somewhat from the unity of the book and, in the reviewer's opinion, might better have been omitted and the space utilised for a somewhat fuller treatment of reaction mechanism, it being granted that this last subject, in its present fluid state, is difficult to come to grips with. This indeed is the only criticism the writer has to offer of an interesting and valuable book.

A. J. Allmand

THE EFFECT OF SALTS ON WEAK ELECTROLYTES*

I. Dissociation of Weak Electrolytes in the Presence of Salts

BY HENRY S. SIMMS

I. Notation and Definitions

The notation used in this article is the same as in a previous paper on the relation of dissociation constants to titration data¹ and a paper on the relation of dissociation constants to chemical structure,² with the exception of the elimination of the "corrected" titration constants (G_1, G_2, G_3 , etc.) which are not true constants under the present assumptions, and a redefinition of τ , which is now defined by the equation

$$\log \tau = a \sqrt{\mu}$$

where

$$a = \text{a constant} = 0.495 \text{ at } 25^\circ\text{C.}$$

$$\mu = \text{ionic strength} = \frac{1}{2} \sum i \nu^2$$

where i is the concentration of a given ion, ν is its valence, and z is a number between 2 and 1 defined by Equation (9).

The term **INDEX** is introduced to refer to the negative logarithm of a number or variable. $-\log X = P_X =$ "Index of X". When X is a type of constant the word "constant" may be omitted:

$$\begin{aligned} P_X &= \text{Dissociation index} \\ P_{G'} &= \text{Titration index} \\ P_H &= \text{H}^+ \text{ ion (activity) index} \\ P_h &= \text{H}^+ \text{ ion (concentration) index.} \end{aligned}$$

An "index unit" (which we formerly called P_H unit) is the logarithm of 10. Thus if $P_{G_1'} = 4.0$ and $P_{G_2'} = 5.5$, the two titration indices are 1.5 *index units* apart.

The following symbols are repeated for convenience:

K_1', K_2', K_3' , etc. = Dissociation constants not corrected for activity.

K_1, K_2, K_3 , etc. = Dissociation constants corrected for activity.

G_1', G_2', G_3' , etc. = Titration constants (uncorrected).

$\alpha_1, \alpha_2, \alpha_3$ = Probabilities of dissociation according to G_1', G_2' , and G_3' , respectively.

u, m, d , and t = Fractions of a substance in the undissociated, mono-ion di-ion and tri-ion forms, respectively.

c, a, b, h , and oh = Molal concentrations of substance, strong acid, strong base, hydrogen ion and hydroxyl ion, respectively.

H and OH = Activities of hydrogen ion and hydroxyl ion, respectively.

"Dissociation" refers to the effect of ionization of acid groups and hydrolysis of the salts of basic (amino) groups. Dissociation indices are designated in order of numerical value, regardless of type of group.

f_0, f_1, f_2 , etc. = Activity coefficients when 0, 1, 2, etc. groups have "dissociated".

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¹ Simms: J. Am. Chem. Soc., 48, 1239 (1926). To be consistent with the present notation and assumptions, section VII of that paper should be omitted; also omit the *fifth* step in section VIII, the last sentence in the *sixth* step and the last clause in the *seventh* step. In Table I, 0.03 should be subtracted from the values in column 5, thus slightly altering the rest of the table.

² Simms: J. Am. Chem. Soc., 48, 1251 (1926).

The following notation is added:

I after the number of an equation signifies that the equation refers only to substances with "isolated" constants (2.5 or more index units apart).

A after the number of an equation indicates that it refers only to acids, B only to bases, and M only to ampholytes.

I or II before the number of an equation in the text refers to an equation in paper I or II, respectively.^{1,2}

Molar concentration refers to mols per 1000 cc. of solution.

II. Introduction

The Debye-Hückel equation has been found to apply fairly accurately to inorganic (strong) electrolytes, although less has been done in extending it to weak electrolytes. It would be expected that those molecules of a weak electrolyte which are ionized should obey this equation. On this assumption Sherrill and Noyes, and also MacInnes³ have successfully applied an activity correction to conductivity data on monovalent weak acids and obtain consistent dissociation constants. Harned⁴ has studied formic acid by catalysis. Hastings and Sendroy⁵ have studied carbonic and phosphoric acids. Cohn⁶ has studied $P_{K'}$ of phosphoric acid. Attempts have been made by Cohn, by Sørensen, and by Stadie⁷ to extend the Debye-Hückel equation to proteins.

However, no systematic study has been made of the activity coefficients of monovalent and polyvalent organic acids, bases and ampholytes. This paper deals with the effect of ionic strength of various salts on the activity coefficients of weak electrolytes as shown by the effect on the dissociation indices.

III. Theory

A. *Monovalent substances.* The mass action expression for a monovalent acid such as acetic acid is:

$$K' = \frac{H A^-}{HA} = H \frac{\alpha}{1 - \alpha} \quad (1)$$

where α (which equals A^-/c) is measured as *concentration* and H is observed as *activity*. The true constant (K) must be expressed entirely in terms of *activity*, hence:

$$K = K' \frac{f_1}{f_0} = H \frac{A^- f_1}{HA f_0} = H \frac{\alpha f_1}{1 - \alpha f_0} \quad (2)$$

In dilute solution we may assume that the ions of the weak acid obey the limiting Debye-Hückel equation

$$-\log f = a \nu^2 \sqrt{\mu} = a \nu^2 \sqrt{\frac{1}{2} \sum i \nu^2} \quad (3)$$

³ Sherrill and Noyes: *J. Am. Chem. Soc.*, **48**, 1861; MacInnes: 2068 (1926).

⁴ Harned: *J. Am. Chem. Soc.*, **49**, 1 (1927).

⁵ Hastings and Sendroy: *J. Biol. Chem.*, **65**, 445 (1925); Sendroy and Hastings: 71, 783 (1927).

⁶ Cohn: *J. Am. Chem. Soc.*, **49**, 173 (1927).

⁷ Cohn: *Physiol. Rev.*, **5**, 349 (1925); Sørensen, Linderstrom-Lang and Lund: *J. Gen. Physiol.*, **8**, 547 (1927); Stadie and Hawes: *J. Biol. Chem.*, **74**, xxxi (1927).

and that the undissociated molecules have unit activity coefficients,⁸ hence

$$f_0/f_1 = \tau \quad (4)$$

and we obtain the following equation for a monovalent weak acid:

$$P_K = P_{K'} + \log \tau = P_{K'} + a \sqrt{\mu} \quad (5)$$

Determination of the P_H of solutions of a weak electrolyte in the presence of known amounts of strong acid or base gives us its "potentiometric titration data" from which we may calculate the dissociation constants as previously described.¹ It is evident from Equation 5 that if we plot $\sqrt{\mu}$, for the various points, against calculated dissociation indices ($P_{K'}$) we should obtain in dilute solutions a straight line curve with a slope equal to $-a$, for a weak acid, and equal to $+a$ for a weak base.⁹ The intercept of this curve with the $P_{K'}$ axis should equal P_K (the true dissociation index).

B. Polyvalent substances.—In the second paper,² Equations II 22, II 23, and II 24 gave the relation between the observed dissociation constants, the intrinsic constants, the internal electrostatic work and the activity coefficients. The corresponding equations for a divalent substance are (we include also the relation to the titration constants):

$$K_1' K_2' = K_0^I K_0^{II} L^{II} (f_0/f_2)^{II} = G_1' G_2' \quad (6)$$

$$K_1' = K_0^I L^I (f_0/f_1)^I + K_0^{II} L^{II} = (f_0/f_1)^{II} G_1' + G_2' \quad (7)$$

$$K_2' = \text{Equation 6 divided by Equation 7}$$

where L , a function of electrostatic work, is defined by Equation II 25. Any observed deviation from these exact expressions should be due to error in the assumptions made in their application.

It will be seen that these dissociation constants are dependent upon the activity coefficient ratios (f_0/f_2) and (f_0/f_1). The Debye-Hückel equation is satisfactory for determining the activity coefficient ratio of monovalent acids; but we must modify the equation before we can deal with the polyvalent acids.

C. Modification of the Debye-Hückel equation to apply to long ions.—The Debye-Hückel equation is derived on the assumption that the charge on an ion is located at a point or on the surface of a sphere. If we should

⁸ In spite of the evidence offered by Randall (Chem. Rev., 4, 291 (1927)) that the activity coefficients of non-ionized molecules differ from unity by a few per cent, we make the working assumption that $f_0 = 1$. We also assume that the coefficients for ions are given by Equations 8 and 9. The error in these ideal assumptions appears as a discrepancy between experimental and calculated values of S .

These discrepancies when converted into differences in activity coefficient ratios in 0.9μ solutions amount to less than 3 per cent in the presence of NaCl; but in the presence of MgCl₂ represent a lowering of 3 to 10 per cent in f_1/f_0 ; 13 to 90 per cent in f_2/f_1 ; and 95 per cent in f_2/f_2 . The effect of K₂SO₄ is to increase f_2/f_1 10 per cent above the calculated value.

It is unwise to assign these deviations to particular ionic species until we have more data on weak electrolytes. Randall's assumption that the weak ions have activities identical with HCl mitigates the accuracy of his resulting calculations.

⁹ See definition of "dissociation" at beginning of article.

have a dianion with charges so far separated that the distance between them is comparable to that between individual ions, it is evident that each should behave like a separate univalent ion. To correct for this distance we may write the limiting equation (3) as follows:¹⁰

$$-\log f = \nu^2 a \sqrt{\frac{1}{2} \sum i \nu^2} = \log \tau^{\nu^2} \quad (8)$$

where z is a number between 1 and 2 such that for a point charge $\nu^2 = \nu^2$ and for an ion with a very long distance between charges $\nu^2 = \nu$. For acids with a maximum distance of r_x Ångström units between the charges we may write as an approximation:¹¹

$$\nu^2 = \nu^2 - (\nu^2 - \nu) r_x / 18 \quad (9)$$

where the probable mean distance between ions is about 18 Å. (r_x must never be assumed greater than 18 Å in this equation.) The agreement of the data with these equations is shown in Fig. 1.

D. Application of modified equation. Let us assume that the ions of a divalent acid obey the *modified* equations (8 and 9) and that the non-ionized molecules have unit activity coefficients ($\nu_0^2 = 0$), then

$$(f_0/f_1)^I = (f_0/f_1)^{II} = \tau^{\nu_1^2 - \nu_0^2} = \tau^{\nu_1^2} = \tau \quad (10A)$$

$$(f_0/f_2)^I = \tau^{\nu_2^2 - \nu_0^2} = \tau^{\nu_2^2} \quad (11A)$$

(For ions with a point charge $\nu_2^2 = 2^2 = 4$)

From the general equations (6 and 7) we get:

¹⁰ The contribution of a weak acid ($\mu_0 = \frac{1}{2} \sum i \nu^2$) to the total ionic strength ($\mu = \mu_0 + \mu_s$ where μ_s is the contribution of salts) is calculated as described in the following paper.

¹¹ The Debye-Hückel equation was derived to apply to such ions as could be considered to have either a point charge, or a multiple charge distributed with spherical symmetry. In other words the equation applies to ions with a spherical field of force. By no stretch of the imagination can the dianion of azelaic acid be so considered. Its field of force is dumb-bell shaped (resulting from the fusion of two spherical fields). Prof. Debye was kind enough (in 1925) to calculate the result of an ellipsoidal field of force (as an approximation to the dumb-bell field) and arrived at equations which in the extreme case of a sphere give the usual limiting equation ($\nu^2 = \nu^2$); and in the opposite extreme case of a very long ellipsoid agree with Equation 8 where $\nu^2 = \nu$.

This agreed with Equation 8 which I had postulated at that time. However, as Prof. Debye pointed out, it is unlikely that a simple relation between ν^2 and the *distance* can be derived on theoretical grounds since the equations are too complex.

It therefore seems justifiable to find an empirical relation. The simplest and most likely assumption is that within a given range ν^2 varies from ν^2 to ν as a linear function of the distance between charges, reaching ν at the effective mean distance between ions. This proved to be so in the entire range of substances studied. The effective mean distance being 18 Å with an ionic strength from 0.01 to 0.1 μ and a weak acid concentration of 0.01 molar. (The average distances between like charges in 0.01 and 0.1 molar solution would be 55 to 25 Å.)

This mean effective distance should be higher than 18 Å in more dilute solution and lower in more concentrated solution. However we are not justified in introducing a correction for concentration until we have obtained supporting data. It should vary as a function of $\sqrt{1/c}$ and should not affect the data much with small changes in concentration.

Equation 9 probably gives too low values of r_x above 15 Å (i.e., the curves of Fig. 1 probably deviate from the straight lines). However it is seen to agree with those data up to 12 Å. The data for sebacic acid (14 Å) were poor and are not published, but they appeared to agree within the experimental error.

$$K_1 = K_o^I L^I + K_o^{II} L^{II} = \frac{K_1}{\tau} = \frac{G_1' + G_2'}{\tau} \quad (12A)$$

$$K_2 = \frac{K_o^I K_o^{II} L^I L^{II}}{K_o^I L^I + K_o^{II} L^{II}} = \frac{K_2'}{\tau^{\nu_2^2 - \nu_1^2}} = \frac{G_1' G_2'}{(G_1' + G_2') \tau^{\nu_2^2 - \nu_1^2}} \quad (13A)$$

(where $\nu_2^2 - \nu_1^2 = 4 - 1 = 3$ for a point charge).

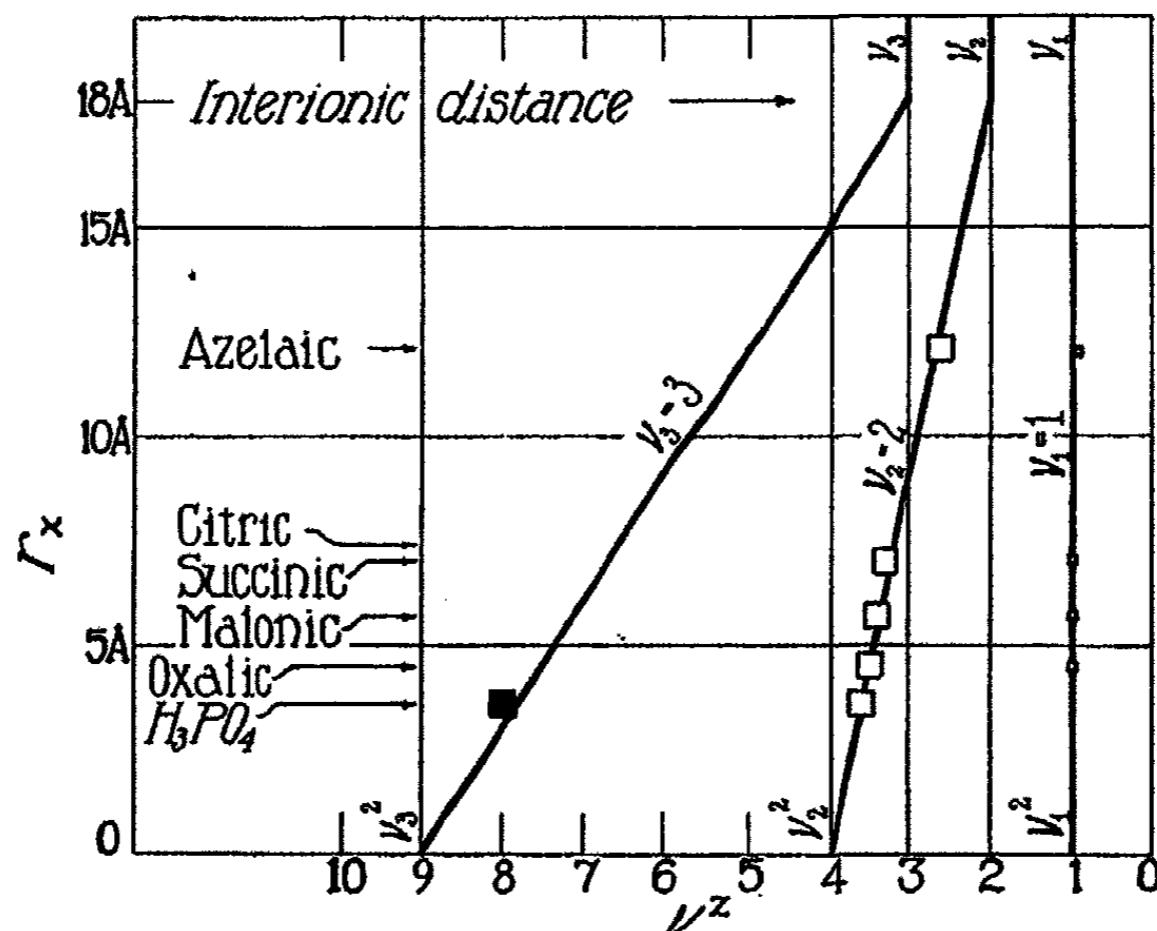


FIG. 1

Plot of values of ν (from data with NaCl) against the distance (r_α) between the negative charges in polyanions. The curves are calculated from equation 9. The small squares are ν_1^2 values. Large squares ν_2^2 values. The solid square is ν_2^2 for H_3PO_4 (data of Sendroy and Hastings).

Similarly for K_3 of a trivalent acid we get:

$$K_3 = \frac{K_3'}{\tau^{\nu_3^2 - \nu_2^2}} \text{ (equal to } \frac{K_3'}{\tau^{9-4}} = \frac{K_3'}{\tau^5} \text{ for a point charge)} \quad (14A)$$

In the case that the constants are "isolated" (more than 2.5 index units apart) these simplify to:

$$K_1 = K_1' / \tau = G_1' / \tau \quad (15AI)$$

$$K_2 = \tau K_2' / \tau^{\nu_2^2 - \nu_1^2} = G_2' / \tau^{\nu_2^2 - \nu_1^2} \quad (16AI)$$

$$K_3 = K_3' / \tau^{\nu_3^2 - \nu_2^2} = G_3' / \tau^{\nu_3^2 - \nu_2^2} \quad (17AI)$$

For a *divalent base* we must substitute $\tau^{\nu_2^2 - \nu_1^2}$ for $1/\tau$ in Equations 12A and 15AI; and τ for $1/\tau^{\nu_2^2 - \nu_1^2}$ in Equations 13A and 16AI.

For a *trivalent base* we must substitute $\tau^{\nu_3^2 - \nu_2^2}$ for $1/\tau$ in Equations 12A and 15AI; and τ for $1/\tau^{\nu_3^2 - \nu_2^2}$ in Equations 14A and 17AI; while $\tau^{\nu_3^2 - \nu_2^2}$ must be substituted for $1/\tau^{\nu_2^2 - \nu_1^2}$ in Equations 13A and 16AI.

For a *divalent (simple) ampholyte* we may write

$$(f^{\circ}/f_1)^I = 1/\tau \text{ and } (f_0/f_1)^{II} = \tau \quad (18M)$$

also $(f_0/f_2) = 1 \quad (19M)$

This gives us unusable equations for overlapping constants, but we may apply the following equations when the constants are "isolated."

$$K_1 = K_1'\tau = G_1\tau' \quad (20MI)$$

$$K_2 = K_2'/\tau = G_2'/\tau' \quad (21MI)$$

All the types of substances discussed in this paper are included in the above discussion except for aspartic acid. P_{K_1}' and P_{K_2}' of this substance should approximately obey the last two equations (above). There will be some error, however, since these constants are not sufficiently isolated. P_{K_3}' should follow Equation 16AI.

In all these equations (10A to 21MI) $\nu_1^{\pm} = 1$, but the values of ν_2^{\pm} and ν_3^{\pm} are to be obtained from Equation 9. Only in the hypothetical (and impossible) case of point charges can the original Debye-Hückel equation be obeyed by di- and trivalent organic ions (giving values of 4 and 9 respectively).

IV. Experimental

We have obtained potentiometric titration data on a number of organic substances, first in the absence of other electrolytes (except the strong acid or base required for titration), second in the presence of two different concentrations of NaCl (0.075 molar and 0.0375 molar), and third in the presence of two different concentrations of MgCl₂ (0.025 molar and 0.0125 molar) having the same respective ionic strengths as the NaCl solutions. The following general procedure was used:

A 0.02 molar solution of the substance (sometimes with 1 or 2 equivalents of NaOH or HCl, depending on conditions) was made up in a 250 cc. volumetric flask. 5 cc. samples were placed in 10 cc. volumetric flasks with the requisite quantities of 0.10 or 0.02 molar NaOH or HCl and with 1 cc. of 0.750 or 0.375 molar NaCl, or 1 cc. of 0.250 or 0.125 molar MgCl₂, or with no salt. The samples were then made up to 10 cc. with distilled water. The P_H values of these solutions were obtained in water-jacketed hydrogen electrode cells¹² at 25.0°C. The cells were used alternately with the different types of solutions, thus eliminating errors in the comparative values. Except where otherwise indicated the final concentration of substance was 0.01 molar. The cells were calibrated against 0.1000 molar HCl (P_H 1.075) at the beginning and end of each day. The liquid junction potential with saturated KCl was assumed constant. The dissociation index of water was taken as 13.890 at 25.0°C. All alkaline solutions containing MgCl₂ which were in the least cloudy were rejected.

¹² Simms: J. Am. Chem. Soc., 45, 2503 (1923).

The "dilution experiments" consisted of a series of P_H measurements on half neutralized ($(b-a)/c = 0.5$) solutions at the various concentrations indicated, all samples being obtained by dilution of the most concentrated solution.

The data are given in Tables II to V. To save space the steps in calculation are omitted from these tables. The method of calculation has been fully described.¹ The data on substances with overlapping constants are given and calculated in the succeeding article. The results, however, are discussed in this paper. The expressions "C.-NaCl" and "D.-NaCl" in these tables refer to data in the presence of 0.075 molar and 0.0375 molar NaCl, respectively. "C.-MgCl₂" and "D.-MgCl₂" refer to 0.025 molar and 0.0125 molar MgCl₂, respectively; C, and D, being abbreviations for concentrated (0.075 μ) and dilute (0.0375 μ).

V. Results

The above data give us dissociation indices (P_K' values) in the absence of salts, in the presence of two concentrations of NaCl, and in the presence of two concentrations of MgCl₂ (with the same respective ionic strengths).

We have calculated the dissociation index from each observation and have plotted \sqrt{u} against P_K' for each constant of each substance (Figures 1 to 5, where circles represent no salt, squares NaCl, diamonds MgCl₂, and triangles dilution data). The slopes of the curves (Sa) are indicated in each case in the presence of NaCl and in the presence of MgCl₂. These are given in the fifth and sixth columns of Table I. The third column gives the slopes predicted if the ions obey the Debye-Hückel equation. The fourth column gives the slopes calculated from equation 9. Note that these agree with the experimental data with NaCl in column 5. The true constant is given in column 2. The observed constant may be expressed in each case by the equation:

$$P_K' = P_K + Sa \sqrt{\mu} \quad (22)$$

The results may be discussed as follows:

The *monovalent acids*. Acetic acid and succinimide have slopes approximately equal to $-a$, indicating that their ions obey the Debye-Hückel equation. The equations for their dissociation indices may be expressed as in Equation 22:

| | | | |
|--------------|-----------------------------------|---------------------------|-------|
| Acetic acid: | $P_K' = 4.740 - 0.9 a \sqrt{\mu}$ | (with NaCl) | (23a) |
| | $P_K' = 4.740 - 1.1 a \sqrt{\mu}$ | (with MgCl ₂) | (23b) |
| Succinimide: | $P_K' = 9.560 - 1.1 a \sqrt{\mu}$ | (with NaCl) | (24a) |
| | $P_K' = 9.560 - 1.3 a \sqrt{\mu}$ | (with MgCl ₂) | (24b) |

Similar equations may be written for all the other substances listed in Table I, but we will not take the space to present them. The value of 4.740 for the true dissociation index of acetic acid agrees well with the extrapolated value (4.748) from MacInnes' calculation of Kendall's conductivity data

TABLE I

Summary of results presented in this and the following paper.

| Substance | P_K | Slope = S_a | | | | ν^2 | | | |
|---------------------------------|-----------------|---------------|------------|------------------------|---------|-------------|--------------|------------|---------------|
| | | with NaCl | | with MgCl ₂ | | | | | |
| | | Debye-Hückel | Equation 9 | Found | Found† | Calculated† | Debye-Hückel | Equation 9 | Found‡ (NaCl) |
| Acetic Acid | 4.740 | -a | -a | -0.9a | -1.1a | | | | |
| Succinimide | 9.560 | -a | -a | -1.1a | -1.3a | | | | |
| Oxalic Acid | P_{K_1} 1.19 | -a | -a | -a | -1.2a | | | | |
| ($r_d = 4.5 \text{ \AA}$) | P_{K_2} 4.22 | -3a | -2.5a | -2.5a | -9a | -6a | 4.0 | 3.5 | 3.5 |
| Malonic Acid* | P_{K_1} 2.89 | -a | -a | -a | -1.1a | | | | |
| ($r_d = 5.7 \text{ \AA}$) | P_{K_2} 5.74 | -3a | -2.4a | -2.4a | -5.5a | -7a | 4.0 | 3.4 | 3.4 |
| Succinic Acid | P_{K_1} 4.195 | -a | -a | -a | -a | | | | |
| ($r_d = 7.0 \text{ \AA}$) | P_{K_2} 5.570 | -3a | -2.2a | -2.3a | -2.8a | (-6a) | 4.0 | 3.2 | 3.3 |
| Azelaic Acid | P_{K_1} 4.525 | -a | -a | -0.9a | -a | | | | |
| ($r_d = 12.1 \text{ \AA}$) | P_{K_2} 5.395 | -3a | -1.65a | -1.7a | -2.0a | (-a) | 4.0 | 2.65 | 2.6 |
| Citric Acid | P_{K_1} 3.08 | -a | -a | | -0.6a | | | | |
| (mean $r_d = 7.4 \text{ \AA}$) | P_{K_2} 4.74 | -3a | -2.3a | | -5.8a | -6a | 4.0 | 3.3 | |
| | P_{K_3} 6.26 | -5a | -3.3a | | -11.2a | -14a | 9.0 | 6.6 | |
| Aminoethanol | 9.470 | +a | +a | +0.47a | +0.05a | | | | |
| Glycine | P_{K_1} 2.365 | +a | +a | -0.08a | -0.08a | | | | |
| | P_I 6.040 | 0 | 0 | (-0.5a) | (-1.6a) | | | | |
| | P_{K_2} 9.715 | -a | -a | -a | -3.2a | | | | |
| Aspartic Acid | P_{K_1} 2.05 | +a | +a | -0.6a | -0.6a | | | | |
| ($r_d = 7.0 \text{ \AA}$) | P_I 2.96 | 0 | 0 | -0.9a | -0.9a | | | | |
| | P_{K_2} 3.87 | -a | -a | -1.2a | -1.2a | | | | |
| | P_{K_3} 10.00 | -3a | -2.2a | -2.3a | -5.9a | -6a | 4.0 | 3.2 | 3.5 |

* Malonic acid was also titrated with K_2SO_4 (S_a equal +0.2a for P_{K_1}' and -2.1a for P_{K_2}') and with $MgSO_4$ (S_a equal -0.2a and -4.5a respectively).

† Since the substances in the presence of $MgCl_2$ were titrated with NaOH the solutions contained both Mg^{++} ions and Na^+ ions. The curve which gives the slope corresponding to only Mg^{++} cations would be drawn through a set of points for $MgCl_2$ and through the points without salt. The values S_x thus obtained for the polyvalent ions with 0.0375μ of $MgCl_2$ are: oxalic, (-1.9); malonic, -10.7; succinic, -3.6; azelaic, -2.5; citric, -11 and -32; and aspartic, -11.7. These correspond roughly to the empirical equation $S_x = 32 + 19 S_0$ (where S_0 is the value with NaCl).

‡ The "calculated" values of S_a in Column 7 are obtained from the empirical equation $S_x = 12.5 + 8 S_0$ (applying only to polyvalent ions). Note that these values agree roughly with those in Column 6.

§ The values of ν^2 in the last column equal $-S_1 - S_2$.

The MONOVALENT BASE aminoethanol has a slope of +0.47a in the presence of NaCl and +0.05a with $MgCl_2$, whereas a slope of +a is required by the Debye-Hückel equation. If the true dissociation index is constant this deviation must be due either to an increased activity of the ions in the presence of salt (which is improbable) or to a decreased activity of the undissociated molecule.

The SIMPLE AMPHOLYTE glycine is represented in Fig. 5. P_{K_1}' shows a similarity to aminoethanol except that the deviation is even greater than in the case of the base, but is about the same with both NaCl and $MgCl_2$.

The difference in action of the two salts is manifested in the P_{K_1}' curves where it behaves like acetic acid in the presence of NaCl, but shows an anomaly with $MgCl_2$.

The DIVALENT ACIDS are represented by four $\alpha\omega$ -dicarboxylic acids, namely, oxalic, malonic, succinic, and azelaic acids. The data are presented in Tables I to IV and Figures 2 to 5 of the subsequent paper. The first dissociation index (P_{K_1}') in each case behaves similarly to acetic acid in the presence of either NaCl or $MgCl_2$.

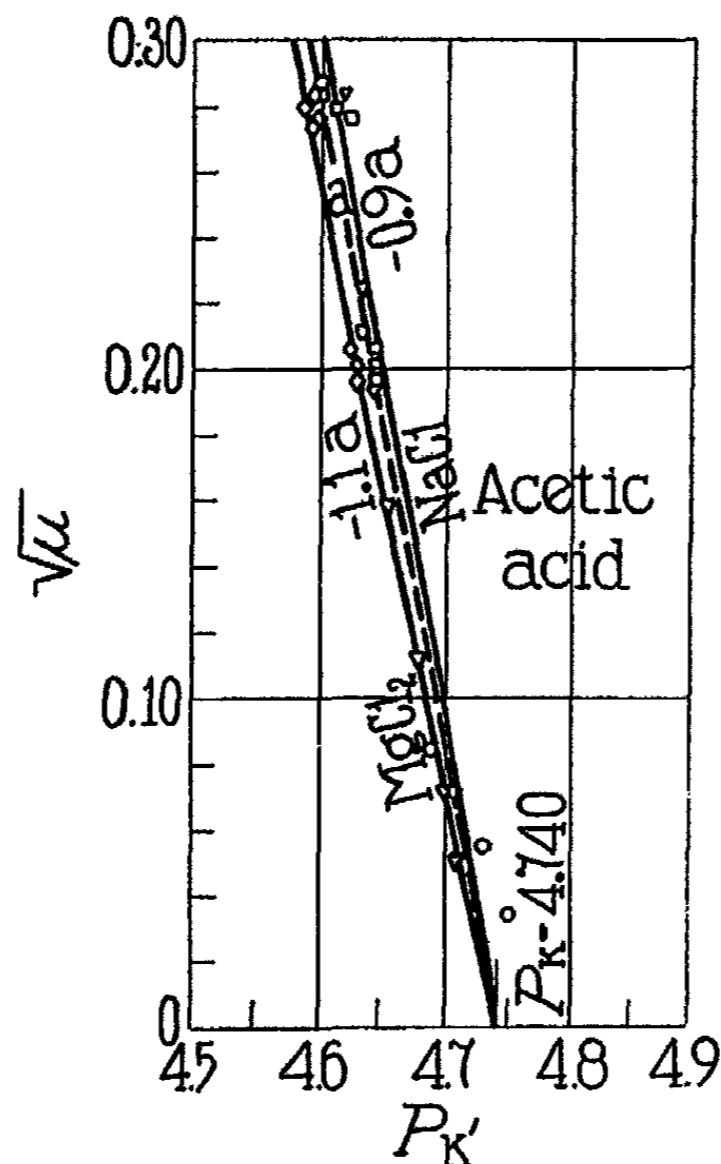


FIG. 2
Acetic Acid

The second dissociation index (P_{K_2}') has a slope in the presence of NaCl less than required by the Debye-Hückel equation, while the slope with $MgCl_2$ is greater than with NaCl in each case. Sebaccic acid behaves similarly to azelaic acid, but its data are not satisfactory for publication.

Curves 1, 2, and 3 of Figure 1 represent the values of ν^* calculated from Equation 9. The observed values (of data with NaCl) are seen to agree within experimental error for ions with 1, 2, or 3 charges. This proves that Equations 8 and 9 may be used as a reasonable approximation of the relation between activity and the distance between charges.

The *long* divalent acids (succinic, azelaic and sebaccic) show a small but definite deviation in the presence of $MgCl_2$, while the *short* acids (oxalic and

malonic) show a very large deviation, as indicated by the large diamonds in Fig. 1 which would fall on the curve of ν_1' if there were no deviation.

The data with MgSO_4 and K_2SO_4 show that the sulfate ion has an effect on both indices of malonic acid which is opposite in direction to the effect of magnesium ions.

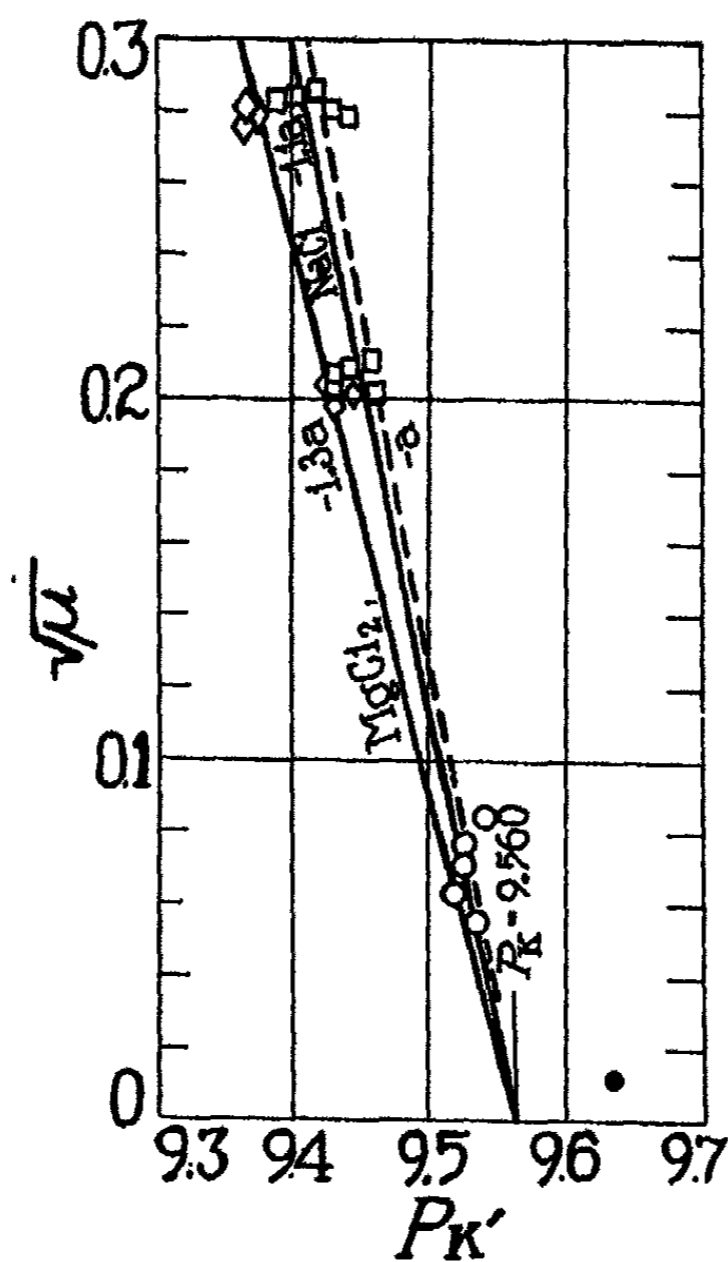


FIG. 3
Succinimide

A TRIVALENT acid, namely citric acid, was studied in the presence of MgCl_2 only. P_{K_1}' , like the first indices of monovalent and divalent acids, obeys the Debye-Hückel equation with MgCl_2 . P_{K_2}' (like that of oxalic and malonic acids) shows a large deviation, while P_{K_3}' shows a still larger deviation, having a slope of $-11.2a$ (not shown in Fig. 1). The slope predicted by equation 9 is $-3.3a$.

A TRIVALENT AMPHOLYTE was studied, namely aspartic acid, which is both an ampholyte and a divalent acid. The first dissociation index (P_{K_1}') behaves like that of glycine. The second (P_{K_2}') behaves like acetic acid and is unlike P_{K_2}' of glycine in that the data with MgCl_2 are normal. The abnormality is not found until we reach the third index (P_{K_3}') where the effects of MgCl_2 and NaCl differ much more than for succinic acid.

VI. Discussion of Anomalies

From the above section and from Table I it will be seen that monovalent acids as well as the monoions of polyvalent acids obey the Debye-Hückel equation either in the presence of $MgCl_2$ or of $NaCl$ (altho not with sulfates). Furthermore, divalent anions obey a modified equation (Equations 8 and 9) in the presence of $NaCl$. (This modified equation involves the distance between charges.)

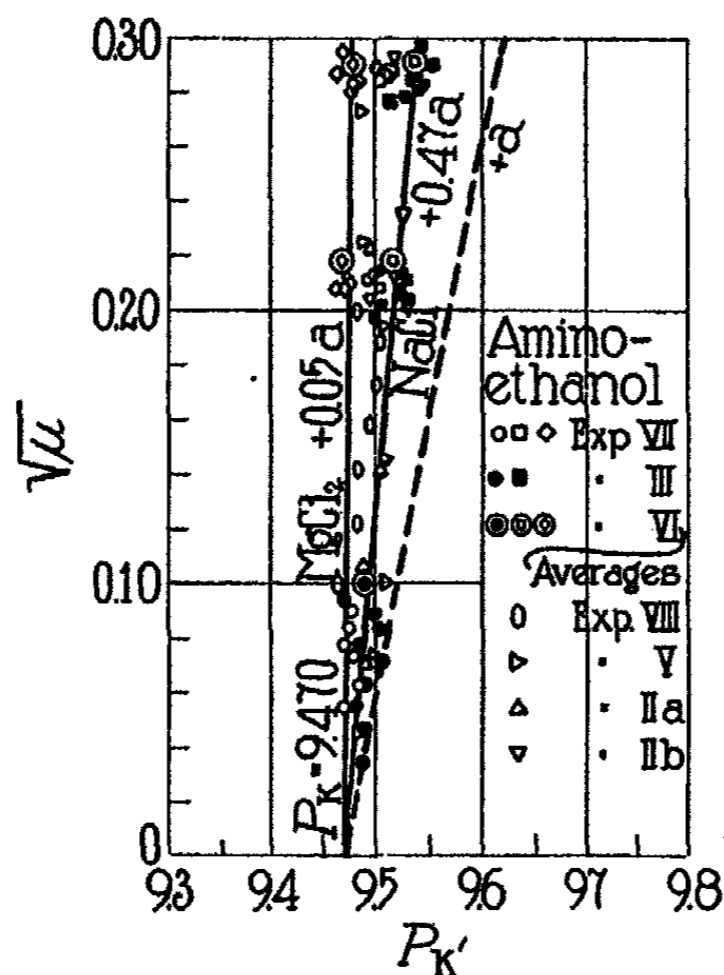


FIG. 4
Aminoethanol

However, there are four anomalies to be found in the data. The first is the *anomalous behavior of cations*. Cations from either amines or ampholytes do not obey the Debye-Hückel equation. Whereas the slopes of the dissociation index of aminoethanol and the first indices of glycine and of aspartic acid should each be $+a$, we find that they are, respectively, $+0.47a$, $-0.08a$, and $-0.6a$ in the presence of $NaCl$; and $-0.05a$, $+0.08a$, and $-0.6a$ in the presence of $MgCl_2$. These deviations involve a shift in the dissociation indices toward the acid side which might signify either that the activity of the ions (RNH_3^+) is too large, or that the non-ionized fraction (RNH_2) has a low activity. In this connection we may refer to the work of Pfeiffer¹³ who isolated complex salts between amino acids, peptides, etc., and inorganic salts and obtained evidence that these exist in solution. Northrop and Kunitz¹⁴ find indication of combinations of ions with proteins.

¹³ Pfeiffer and Wittha: Ber., 48, 1289; Pfeiffer, Würgler and Wittha: 1938 (1915); Z. physik. Chem., 133, 22; 134, 180; 135, 16; 143, 265 (1924).

¹⁴ Northrop and Kunitz: J. Gen. Physiol., 9, 351 (1926) and unpublished data.

The second anomaly is in the effect of $MgCl_2$ on ampholytes, namely on the second dissociation index ($P_{K_2'}$) of glycine and also on the third index ($P_{K_3'}$) of aspartic acid. Both these indices behave normally with NaCl. The index of glycine represents the change from a neutral molecule to an anion. That of aspartic acid represents a change from monoanion to dianion. They have one thing in common, namely, that they represent a change from an amphion (zwitterion) form in neutral solution to a normal form in alkaline solution.

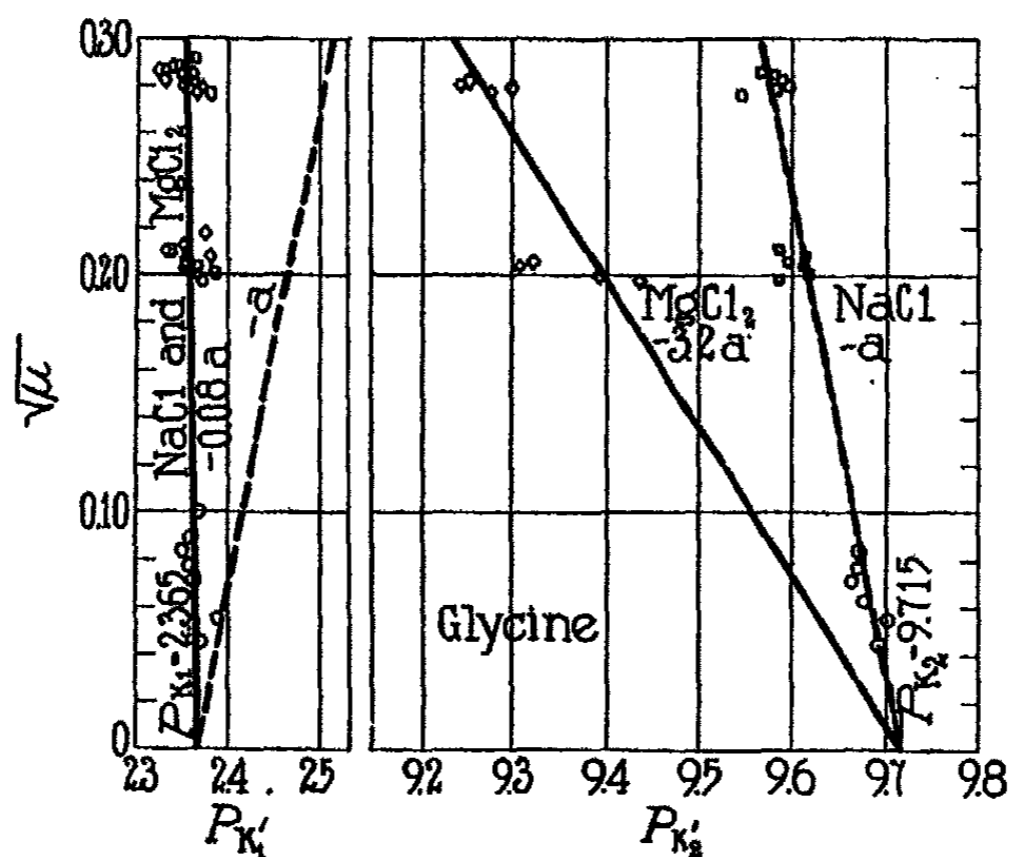


FIG. 5
Glycine

The isoelectric point ($P_I = 6.040$) has a slope of $-0.5a$ with NaCl and $-1.6a$ with $MgCl_2$.

The third anomaly is in the effect of $MgCl_2$ on the second and third indices ($P_{K_2'}$ and $P_{K_3'}$) of divalent and trivalent acids, as shown by the difference between the slopes with NaCl and $MgCl_2$ (see Figures 2 to 6 in the following article, and Table I and Fig. 1 of this paper). The effect is small with long chain acids (succinic, azelaic and sebacic) but is large for oxalic, malonic and citric acids. In this connection we may refer to the deviations observed by Brønsted and LaMer¹⁵ with salts of higher valence type, which Bjerrum and also LaMer and Mason¹⁶ attribute in more recent studies to neglect of higher terms in deriving the Debye-Hückel equation. We may refer also to the high solubility of $CaCO_3$ in phosphate and citrate solutions observed by Hastings, Murray and Sendroy.¹⁷ The high concentration of calcium in the blood was thought by Holt, LaMer and Chown¹⁸ to be due to supersaturation

¹⁵ Brønsted and LaMer: J. Am. Chem. Soc., 46, 555 (1924).

¹⁶ LaMer and Mason: J. Am. Chem. Soc., 49, 410 (1927).

¹⁷ Hastings, Murray and Sendroy: J. Biol. Chem., 71, 723 (1927).

¹⁸ Holt, La Mer and Chown: J. Biol. Chem., 64, 509, 567 (1925).

but Hastings and Sendroy¹⁹ explain it as a combination with other constituents in the serum.

The fourth anomaly is the *effect of sulphate ion*. The data on malonic acid in the presence of MgSO_4 and K_2SO_4 indicate an effect different from the corresponding chlorides but opposite in direction from the effect of the magnesium ion. This deviation is shown by both mono- and dianions.

We will not attempt to explain any of the anomalies. More data are being obtained which have a bearing on this question.

The direction of all the deviations observed in this paper (with the exception of the effect of SO_4 ions) is to render the solutions more acid than expected.

It is interesting to note that the curves for $P_{K_1'}$, $P_{K_2'}$, and $P_{K_3'}$ of polyvalent acids and ampholytes approach each other at higher ionic strengths particularly in the presence of MgCl_2 . Should the same laws hold at higher concentrations we would have $K_3' > K_2' > K_1'$ which is the reverse of the usual relation. This would mean for a polyvalent acid that the ions of higher charge would form more readily. Such a condition may be experimentally possible with oxalic or citric acid. For an ampholyte it would mean that the zwitterions would be supplanted by nonionized molecules.

TABLE II A
Acetic Acid (0.0100 molar)

| Salt | P_H | $\frac{b-a}{c}$ | b' | $P_{K'}$ | $\sqrt{\mu}$ |
|----------------------|-------|-----------------|-------|----------|--------------|
| C. - MgCl_2 | 3.332 | 0 | 0.051 | 4.594 | 0.274 |
| D. - MgCl_2 | 3.350 | 0 | .051 | (4.612) | .194 |
| No salt | 3.394 | 0 | .041 | 4.756 | .020 |
| D. - NaCl | 3.352 | 0 | .051 | (4.614) | .194 |
| C. - NaCl | 3.342 | 0 | .054 | (4.566) | .274 |
| C. - MgCl_2 | 3.742 | 0.100 | .122 | 4.597 | .276 |
| D. - MgCl_2 | 3.766 | .100 | .120 | 4.629 | .196 |
| No salt | 3.864 | .100 | .114 | 4.751 | .034 |
| D. - NaCl | 3.780 | .100 | .119 | 4.645 | .196 |
| C. - NaCl | 3.761 | .100 | .120 | 4.624 | .276 |
| C. - MgCl_2 | 4.238 | .300 | .307 | 4.588 | .279 |
| D. - MgCl_2 | 4.276 | .300 | .306 | 4.629 | .201 |
| No salt | 4.372 | .300 | .304 | 4.729 | .055 |
| D. - NaCl | 4.293 | .300 | .306 | 4.646 | .201 |
| C. - NaCl | 4.260 | .300 | .306 | 4.613 | .279 |
| C. - MgCl_2 | 4.601 | .500 | .503 | 4.594 | .283 |
| D. - MgCl_2 | 4.631 | .500 | .503 | 4.624 | .206 |
| No salt | 4.715 | .500 | .502 | 4.709 | .071 |
| D. - NaCl | 4.631 | .500 | .503 | 4.624 | .206 |
| C. - NaCl | 4.609 | .500 | .503 | 4.602 | .283 |
| C. - MgCl_2 | 4.944 | .700 | .701 | (4.571) | .286 |
| D. - MgCl_2 | 4.983 | .700 | .701 | (4.610) | .211 |
| No salt | 5.063 | .700 | .701 | 4.690 | .084 |
| D. - NaCl | 5.008 | .700 | .701 | 4.635 | .211 |
| C. - NaCl | 4.971 | .700 | .701 | 4.598 | .286 |
| No salt | 6.768 | 1.000 | 1.000 | | |

¹⁹ Hastings and Sendroy: J. Biol. Chem., 71, 723 (1927).

It will be observed that the isoelectric point is dependent upon ionic strength. More information as to the cause of this deviation must be obtained before we can accept the theory of Sørensen⁷ that a constant "isoionic" point exists. This theory necessitates that the deviation is due to the substitution of H⁺ ion by another cation producing a weakly ionized salt. This is not consistent with some of our (unpublished) data.

TABLE II B
Acetic Acid at Various Dilutions—Half Neutralized $\frac{b-a}{c} = 0.5$

| <i>c</i> | <i>P_H</i> | <i>b'</i> | <i>P_{K'}</i> | $\sqrt{\mu}$ |
|----------|----------------------|-----------|-----------------------|--------------|
| 0.160 | 4.619 | 0.500 | 4.619 | 0.283 |
| .100 | 4.636 | .500 | 4.636 | .224 |
| .075 | 4.644 | .500 | 4.644 | .194 |
| .050 | 4.660 | .500 | 4.660 | .158 |
| .025 | 4.680 | .501 | 4.678 | .112 |
| .010 | 4.705 | .502 | 4.701 | .071 |
| .005 | 4.717 | .504 | 4.709 | .050 |

TABLE III
Succinimide (0.0112 and 0.0123 molar*)
The data plotted in Figure 3 were lost. These data are less accurate.

| Salt | <i>P_H</i> | $\frac{b-a}{c}$ | <i>b'</i> | <i>P_{K'}</i> | $\sqrt{\mu}$ |
|----------------------|----------------------|-----------------|-----------|-----------------------|--------------|
| C.—MgCl ₂ | 8.695 | 0.178 | 0.178 | 9.358 | 0.277 |
| D.—MgCl ₂ | 8.756 | .178 | .178 | 9.419 | .199 |
| No salt | (8.83) | .178 | .178 | (9.49) | .045 |
| D.—NaCl | 8.751 | .178 | .178 | 9.413 | .199 |
| C.—NaCl | 8.724 | .178 | .178 | (9.487) | .277 |
| C.—MgCl ₂ | 8.911 | .268 | .267 | 9.349 | .279 |
| D.—MgCl ₂ | 8.966 | .268 | .267 | 9.404 | .201 |
| No salt | 9.097 | .268 | .267 | 9.537 | .055 |
| D.—NaCl | (8.96) | .268 | .267 | (9.40) | .201 |
| C.—NaCl | 8.930 | .268 | .267 | 9.370 | .279 |
| No salt | 9.260 | .357 | .356 | 9.518 | .063 |
| D.—NaCl | 9.175 | .357 | .356 | 9.433 | .204 |
| C.—NaCl | 9.137 | .357 | .356 | 9.393 | .281 |
| No salt | 9.426 | .446 | .445 | 9.525 | .071 |
| D.—NaCl | 9.323 | .446 | .445 | 9.421 | .206 |
| C.—NaCl | 9.290 | .446 | .445 | 9.388 | .283 |
| No salt | 9.509 | .488* | .485 | 9.535 | .077 |
| D.—NaCl | 9.423 | .488* | .485 | 9.449 | .208 |
| C.—NaCl | 9.380 | .488* | .485 | 9.406 | .285 |
| C.—MgCl ₂ | 9.529 | .569* | .564 | 9.417 | .286 |
| D.—MgCl ₂ | 9.578 | .569* | .564 | 9.466 | .211 |
| No salt | 9.625 | .569* | .564 | 9.513 | .084 |
| D.—NaCl | 9.585 | .569* | .564 | 9.473 | .211 |
| C.—NaCl | 9.539 | .569* | .564 | 9.427 | .286 |
| C.—MgCl ₂ | 9.679 | .650* | .644 | 9.421 | .288 |
| D.—MgCl ₂ | 9.737 | .650* | .644 | (9.479) | .213 |
| No salt | 9.776 | .650* | .644 | 9.518 | .089 |
| D.—NaCl | 9.752 | .650* | .644 | (9.494) | .213 |
| C.—NaCl | 9.708 | .650* | .644 | 9.450 | .288 |

* The concentration of solutions marked with an asterisk was 0.0123 molar. The other solutions were 0.0112 molar.

TABLE IVA
Aminoethanol (0.0100 molar) Experiment VII

| Salt | P_H | $\frac{b-a}{c}$ | b' | $P_{K'}$ | $\sqrt{\mu}$ |
|------------------------|-------|-----------------|--------|----------|--------------|
| No salt | 3.032 | -1.100 | -1.007 | | |
| No salt | 4.82 | -1.000 | -.998 | | |
| C. - MgCl ₂ | 8.515 | -.900 | -.900 | 9.470 | 0.290 |
| D. - MgCl ₂ | 8.519 | -.900 | -.900 | 9.474 | .216 |
| No salt | 8.482 | -.900 | -.900 | (9.437) | .095 |
| D. - NaCl | 8.53 | -.900 | -.900 | (9.54) | .216 |
| C. - NaCl | 8.536 | -.900 | -.900 | (9.491) | .290 |
| C. - MgCl ₂ | 8.744 | -.850 | -.851 | 9.502 | .289 |
| D. - MgCl ₂ | 8.746 | -.850 | -.851 | 9.504 | .214 |
| C. - MgCl ₂ | 8.876 | -.800 | -.801 | 9.481 | .288 |
| D. - MgCl ₂ | 8.872 | -.800 | -.801 | 9.477 | .213 |
| No salt | 8.874 | -.800 | -.801 | 9.479 | .090 |
| D. - NaCl | 8.893 | -.800 | -.801 | 9.498 | .213 |
| C. - NaCl | 8.909 | -.800 | -.801 | 9.514 | .288 |
| C. - MgCl ₂ | 8.984 | -.750 | -.751 | 9.464 | .287 |
| D. - MgCl ₂ | 8.984 | -.750 | -.751 | 9.464 | .212 |
| C. - MgCl ₂ | 9.101 | -.700 | -.702 | 9.474 | .286 |
| D. - MgCl ₂ | 9.099 | -.700 | -.702 | 9.472 | .211 |
| No salt | 9.103 | -.700 | -.702 | 9.476 | .084 |
| D. - NaCl | 9.121 | -.700 | -.702 | 9.494 | .211 |
| C. - NaCl | 9.135 | -.700 | -.702 | 9.508 | .286 |
| C. - MgCl ₂ | 9.306 | -.600 | -.602 | 9.486 | .285 |
| D. - MgCl ₂ | 9.283 | -.600 | -.602 | 9.463 | .208 |
| No salt | 9.290 | -.600 | -.603 | 9.472 | .078 |
| D. - NaCl | 9.323 | -.600 | -.603 | 9.505 | .208 |
| C. - NaCl | 9.323 | -.600 | -.603 | 9.505 | .285 |
| No salt | 9.473 | -.500 | -.504 | 9.480 | .074 |
| D. - NaCl | 9.497 | -.500 | -.504 | 9.504 | .206 |
| C. - NaCl | 9.519 | -.500 | -.504 | 9.526 | .283 |
| No salt | 9.652 | -.400 | -.406 | 9.486 | .063 |
| D. - NaCl | 9.679 | -.400 | -.406 | 9.513 | .204 |
| C. - NaCl | 9.693 | -.400 | -.406 | 9.527 | .281 |
| No salt | 9.820 | -.300 | -.309 | 9.470 | .055 |
| D. - NaCl | 9.844 | -.300 | -.309 | 9.494 | .201 |
| C. - NaCl | 9.863 | -.300 | -.309 | 9.513 | .279 |

TABLE IV B
Aminoethanol (0.0102 molar) Experiment III

| Salt | P_H | $\frac{b-a}{c}$ | b' | P_K' | $\sqrt{\mu}$ |
|---------|--------|-----------------|--------|---------|--------------|
| No salt | 10.633 | 0 | -0.054 | (9.5) | 0.023 |
| No salt | 10.264 | -0.098 | -.121 | (9.399) | .035 |
| D.-NaCl | 10.302 | -.098 | -.124 | (9.452) | .196 |
| C.-NaCl | 10.302 | -.098 | -.124 | (9.452) | .275 |
| No salt | 10.066 | -.196 | -.211 | 9.491 | .047 |
| D.-NaCl | 10.075 | -.196 | -.211 | 9.499 | .199 |
| C.-NaCl | 10.088 | -.196 | -.212 | 9.515 | .277 |
| No salt | 9.847 | -.294 | -.303 | 9.483 | .056 |
| D.-NaCl | 9.876 | -.294 | -.304 | 9.516 | .201 |
| C.-NaCl | 9.888 | -.294 | -.304 | 9.528 | .279 |
| No salt | 9.673 | -.392 | -.398 | 9.492 | .064 |
| D.-NaCl | 9.708 | -.392 | -.399 | 9.529 | .204 |
| C.-NaCl | 9.722 | -.392 | -.399 | 9.543 | .281 |
| No salt | 9.517 | -.490 | -.494 | 9.507 | .071 |
| D.-NaCl | 9.534 | -.490 | -.494 | 9.524 | .206 |
| C.-NaCl | 9.554 | -.490 | -.495 | 9.545 | .283 |
| No salt | 9.331 | -.588 | -.591 | 9.487 | .078 |
| D.-NaCl | 9.368 | -.588 | -.591 | 9.524 | .208 |
| C.-NaCl | 9.381 | -.588 | -.591 | 9.537 | .285 |
| No salt | 9.162 | -.686 | -.688 | 9.505 | .083 |
| D.-NaCl | 9.187 | -.686 | -.688 | 9.530 | .211 |
| C.-NaCl | 9.199 | -.686 | -.688 | 9.542 | .286 |
| No salt | 8.939 | -.784 | -.785 | 9.501 | .089 |
| D.-NaCl | 8.964 | -.784 | -.785 | 9.526 | .213 |
| C.-NaCl | 8.981 | -.784 | -.785 | 9.543 | .288 |
| No salt | 8.600 | -.882 | -.883 | (9.472) | .095 |
| D.-NaCl | 8.632 | -.882 | -.883 | 9.506 | .215 |
| C.-NaCl | 8.629 | -.882 | -.883 | 9.503 | .290 |
| No salt | 7.615 | -.980 | -.980 | | |
| No salt | 3.198 | -1.016 | -1.016 | | |

TABLE IV C
 Aminoethanol Hydrochloride (0.0100 molar) Experiment VI
 ($\frac{b-a}{c}$ of mother solution = -1.00)

| Salt | P_H | $\frac{b-a}{c}$ | b' | $P_{K'}$ | $\sqrt{\mu}$ |
|-----------------------|--------|-----------------|--------|----------|--------------|
| No salt | 8.871 | -0.800 | -0.801 | 9.476 | 0.100 |
| " " | 9.120 | -.700 | -.702 | 9.493 | .100 |
| " " | 9.321 | -.600 | -.603 | 9.502 | .100 |
| " " | 9.485 | -.500 | -.504 | 9.491 | .100 |
| " " | 9.835 | -.300 | -.309 | 9.485 | .100 |
| No salt | 9.113 | -.700 | -.702 | 9.486 | .100 |
| " " | 9.317 | -.600 | -.603 | 9.498 | .100 |
| " " | 9.485 | -.500 | -.504 | 9.491 | .100 |
| " " | 9.670 | -.400 | -.406 | 9.504 | .100 |
| " " | 9.840 | -.300 | -.309 | 9.490 | .100 |
| D. -NaCl | 8.551 | -.900 | -.901 | 9.510 | .218 |
| C. -NaCl | 8.571 | -.900 | -.901 | 9.530 | .291 |
| D. -NaCl | 8.913 | -.800 | -.801 | 9.518 | .218 |
| C. -NaCl | 8.939 | -.800 | -.801 | 9.544 | .291 |
| D. -NaCl | 9.155 | -.700 | -.702 | 9.530 | .218 |
| C. -NaCl | 9.180 | -.700 | -.702 | 9.553 | .291 |
| D. -NaCl | 9.333 | -.600 | -.603 | 9.515 | .218 |
| C. -NaCl | 9.353 | -.600 | -.603 | 9.533 | .291 |
| D. -NaCl | 9.511 | -.500 | -.504 | 9.518 | .218 |
| C. -NaCl | 9.534 | -.500 | -.504 | 9.541 | .291 |
| D. -NaCl | 9.683 | -.400 | -.407 | 9.519 | .218 |
| C. -NaCl | 9.698 | -.400 | -.408 | 9.536 | .291 |
| D. -NaCl | 9.864 | -.300 | -.311 | 9.518 | .218 |
| C. -NaCl | 9.881 | -.300 | -.312 | 9.538 | .291 |
| D. -NaCl | 10.061 | -.200 | -.217 | 9.504 | .218 |
| C. -NaCl | 10.086 | -.200 | -.218 | 9.532 | .291 |
| D. -MgCl ₂ | 8.471 | -.900 | -.900 | (9.426) | .218 |
| C. -MgCl ₂ | 8.488 | -.900 | -.900 | (9.443) | .291 |
| D. -MgCl ₂ | 8.702 | -.850 | -.850 | 9.456 | .218 |
| C. -MgCl ₂ | 8.713 | -.850 | -.850 | 9.467 | .291 |
| D. -MgCl ₂ | 8.884 | -.800 | -.800 | 9.486 | .218 |
| C. -MgCl ₂ | 8.881 | -.800 | -.800 | 9.483 | .291 |
| D. -MgCl ₂ | 8.971 | -.750 | -.751 | 9.451 | .218 |
| C. -MgCl ₂ | 9.001 | -.750 | -.751 | 9.481 | .291 |
| D. -MgCl ₂ | 9.108 | -.700 | -.702 | 9.481 | .218 |
| C. -MgCl ₂ | 9.111 | -.700 | -.702 | 9.484 | .291 |

Average values:

| Salt | $P_{K'}$ | $\sqrt{\mu}$ |
|-----------------------|----------|--------------|
| No salt | 9.492 | 0.100 |
| D. -NaCl | 9.517 | .218 |
| C. -NaCl | 9.538 | .291 |
| D. -MgCl ₂ | 9.469 | .218 |
| C. -MgCl ₂ | 9.479 | .291 |

TABLE IV D
Aminoethanol (0.0488 molar) Experiment VIII. (Higher Concentration)

| P_H | $\frac{b-a}{c}$ | b' | $P_{a'}$ | $\sqrt{\mu}$ |
|--------|-----------------|--------|----------|--------------|
| 10.93 | 0 | -0.022 | | |
| 10.045 | -0.205 | -.208 | 9.465 | 0.100 |
| 9.834 | -.307 | -.309 | 9.484 | .122 |
| 9.636 | -.410 | -.414 | 9.484 | .141 |
| 9.471 | -.514 | -.515 | 9.496 | .158 |
| 9.280 | -.615 | -.615 | 9.502 | .173 |
| 9.101 | -.717 | -.717 | 9.507 | .188 |
| 8.823 | -.820 | -.820 | 9.483 | .200 |
| 2.88 | -1.025 | -1.000 | | |

TABLE IV E
Aminoethanol at various concentrations—half neutralized ($\frac{b-a}{c} = -0.5$)

| | c | P_H | b' | $P_{z'}$ | $\sqrt{\mu}$ |
|-----------|-------|---------|--------|----------|--------------|
| | 0.200 | 9.467 | -0.500 | (9.467) | 0.316 |
| | .100 | 9.497 | -.500 | 9.497 | .223 |
| Exp. II a | .040 | 9.504 | -.501 | 9.506 | .141 |
| | .020 | 9.486 | -.502 | 9.490 | .100 |
| | .010 | 9.486 | -.503 | 9.492 | .071 |
| | .004 | 9.424 | -.507 | (9.437) | .045 |
| | .002 | 9.407 | -.504 | (9.440) | .032 |
| Exp. II b | .180 | 9.483 | -.504 | 9.489 | .505 |
| with | .089 | 9.512 | -.504 | 9.518 | .415 |
| C. - NaCl | .036 | 9.521 | -.504 | 9.527 | .333 |
| | .018 | 9.512 | -.504 | 9.518 | .305 |
| | .009 | 9.491 | -.504 | 9.497 | .288 |
| Exp. V | .200 | (9.500) | -.500 | (9.500) | .316 |
| | .150 | 9.489 | -.500 | 9.489 | .274 |
| | .100 | 9.491 | -.500 | 9.491 | .223 |
| | .075 | 9.508 | -.501 | 9.509 | .194 |
| | .040 | 9.508 | -.501 | 9.509 | .141 |
| | .020 | 9.508 | -.502 | 9.511 | .100 |
| | .010 | 9.491 | -.504 | 9.498 | .071 |
| | .004 | 9.466 | -.510 | 9.483 | .045 |

TABLE V A
 Glycine (0.0100 molar) Acid titration

| Salt | P_H | $\frac{b-a}{c}$ | b' | $P_{K'}$ | $\sqrt{\mu}$ |
|------------------------|-------|-----------------|--------|----------|--------------|
| C. - MgCl ₂ | 2.357 | -1.000 | -0.500 | 2.357 | 0.292 |
| D. - MgCl ₂ | 2.357 | -1.000 | -.510 | 2.374 | .218 |
| No salt | 2.350 | -1.000 | -.510 | 2.367 | .100 |
| D. - NaCl | 2.357 | -1.000 | -.510 | 2.374 | .218 |
| C. - NaCl | 2.360 | -1.000 | -.500 | 2.360 | .292 |
| C. - MgCl ₂ | 2.479 | -0.800 | -.420 | 2.338 | .288 |
| D. - MgCl ₂ | 2.475 | -.800 | -.429 | 2.350 | .213 |
| No salt | 2.469 | -.800 | -.437 | 2.359 | .089 |
| D. - NaCl | 2.477 | -.800 | -.429 | 2.352 | .213 |
| C. - NaCl | 2.484 | -.800 | -.420 | 2.344 | .288 |
| C. - MgCl ₂ | 2.550 | -.700 | -.373 | 2.324 | .286 |
| D. - MgCl ₂ | 2.546 | -.700 | -.380 | 2.333 | .211 |
| No salt | 2.541 | -.700 | -.391 | 2.350 | .084 |
| D. - NaCl | 2.550 | -.700 | -.380 | 2.337 | .211 |
| C. - NaCl | 2.553 | -.700 | -.373 | 2.326 | .286 |
| C. - MgCl ₂ | 2.643 | -.600 | -.343 | 2.360 | .285 |
| D. - MgCl ₂ | 2.643 | -.600 | -.343 | 2.380 | .208 |
| No salt | 2.628 | -.600 | -.349 | 2.357 | .077 |
| D. - NaCl | 2.640 | -.600 | -.343 | 2.357 | .208 |
| C. - NaCl | 2.640 | -.600 | -.333 | 2.346 | .285 |
| C. - MgCl ₂ | 2.729 | -.500 | -.285 | 2.329 | .283 |
| D. - MgCl ₂ | 2.714 | -.500 | -.280 | (2.303) | .206 |
| No salt | 2.726 | -.500 | -.302 | 2.361 | .071 |
| D. - NaCl | 2.736 | -.500 | -.294 | 2.355 | .206 |
| C. - NaCl | 2.739 | -.500 | -.290 | 2.349 | .283 |
| C. - MgCl ₂ | 2.854 | -.400 | -.238 | 2.348 | .281 |
| D. - MgCl ₂ | 2.853 | -.400 | -.241 | 2.353 | .204 |
| No salt | 2.843 | -.400 | -.249 | 2.363 | .063 |
| D. - NaCl | 2.856 | -.400 | -.245 | 2.366 | .204 |
| C. - NaCl | 2.861 | -.400 | -.241 | 2.362 | .281 |
| C. - MgCl ₂ | 3.007 | -.300 | -.188 | 2.371 | .279 |
| D. - MgCl ₂ | 3.000 | -.300 | -.188 | 2.365 | .201 |
| No salt | 2.996 | -.300 | -.198 | (2.389) | .055 |
| D. - NaCl | 3.012 | -.300 | -.191 | 2.386 | .201 |
| C. - NaCl | 3.022 | -.300 | -.191 | (2.396) | .279 |
| C. - MgCl ₂ | 3.198 | -.200 | -.128 | 2.365 | .277 |
| D. - MgCl ₂ | 3.186 | -.200 | -.128 | 2.353 | .199 |
| No salt | 3.178 | -.200 | -.132 | 2.369 | .045 |
| D. - NaCl | 3.196 | -.200 | -.129 | 2.366 | .199 |
| C. - NaCl | 3.210 | -.200 | -.129 | 2.380 | .277 |
| No salt | 7.1 | 0 | | | |

TABLE V B
 Glycine (0.0100 molar) Alkaline titration

| Salt | P_H | $\frac{b-a}{c}$ | b' | P_{K_1}' | $\sqrt{\mu}$ |
|------------------------|--------|-----------------|-------|------------|--------------|
| C. - MgCl ₂ | 8.671 | 0.200 | 0.199 | 9.276 | 0.277 |
| D. - MgCl ₂ | 8.830 | .200 | .199 | 9.435 | .199 |
| No salt | 9.087 | .200 | .198 | 9.694 | .045 |
| D. - NaCl | 8.979 | .200 | .199 | 9.584 | .199 |
| C. - NaCl | 8.942 | .200 | .199 | 9.547 | .277 |
| C. - MgCl ₂ | 8.930 | .300 | .299 | 9.301 | .279 |
| D. - MgCl ₂ | 9.020 | .300 | .298 | 9.393 | .201 |
| No salt | 9.326 | .300 | .297 | 9.701 | .055 |
| D. - NaCl | 9.240 | .300 | .297 | 9.615 | .201 |
| C. - NaCl | 9.209 | .300 | .297 | 9.584 | .279 |
| C. - MgCl ₂ | 9.065 | .400 | .398 | 9.245 | .281 |
| D. - MgCl ₂ | 9.128 | .400 | .398 | 9.308 | .204 |
| No salt | 9.494 | .400 | .396 | 9.678 | .063 |
| D. - NaCl | 9.427 | .400 | .396 | 9.611 | .204 |
| C. - NaCl | 9.409 | .400 | .396 | 9.593 | .281 |
| C. - MgCl ₂ | 9.248 | .500 | .497 | 9.253 | .283 |
| D. - MgCl ₂ | 9.316 | .500 | .497 | 9.323 | .206 |
| No salt | 9.653 | .500 | .494 | 9.663 | .071 |
| D. - NaCl | 9.583 | .500 | .494 | 9.593 | .206 |
| C. - NaCl | 9.578 | .500 | .494 | 9.588 | .283 |
| C. - MgCl ₂ | 9.240 | .600 | .597 | 9.079 | .285 |
| D. - MgCl ₂ | 9.337 | .600 | .597 | 9.166 | .208 |
| No salt | 9.832 | .600 | .591 | 9.671 | .077 |
| D. - NaCl | 9.773 | .600 | .591 | 9.612 | .208 |
| C. - NaCl | 9.742 | .600 | .591 | 9.581 | .285 |
| No salt | 10.011 | .700 | .686 | 9.671 | .084 |
| D. - NaCl | 9.927 | .700 | .687 | 9.585 | .211 |
| C. - NaCl | 9.910 | .700 | .687 | 9.568 | .286 |
| No salt | 10.178 | .800 | .779 | 9.631 | .089 |
| D. - NaCl | 10.102 | .800 | .781 | 9.550 | .213 |
| C. - NaCl | 10.077 | .800 | .781 | 9.525 | .288 |
| No salt | 10.622 | 1.000 | .941 | 9.416 | .100 |
| D. - NaCl | 10.525 | 1.000 | .949 | 9.355 | .218 |
| C. - NaCl | 10.513 | 1.000 | .948 | 9.252 | .292 |

VII. Summary

Titration data of 0.01 molar solutions of various organic acids, bases and ampholytes were obtained, in the absence of salt, in the presence of two concentrations of NaCl, and in the presence of two concentrations of MgCl₂. (K₂SO₄ and MgSO₄ were also used with malonic acid.) From each observation a dissociation index value (P_{K_1}') was calculated and plotted against the square root of the ionic strength ($\sqrt{\mu}$). The slopes of these curves show the extent of agreement of the activity of the ions with the activities predicted by the Debye-Hückel equation. The true dissociation indices and the slopes are given in Table I.

Singly charged anions from monovalent or divalent acids obey the Debye-Hückel equation in the presence of either NaCl or MgCl₂, or the salt of the weak acid, but not with K₂SO₄ or MgSO₄.

Polyvalent anions in the presence of NaCl obey a modified form of this equation which includes a correction for the distance between the charges (Equations 8 and 9).

Polyvalent anions behave anomalously with $MgCl_2$. This effect is much greater for oxalic, malonic, and citric acids than for succinic, azelaic and sebacic acids.

Sulfate ions produce an effect on both mono- and dianions which is opposite to the effect of magnesium ions.

Cations from amines or amino acids do not obey the Debye-Hückel equation but show a deviation with both NaCl and $MgCl_2$, which varies with the substance.

P_{K_2}' of glycine and P_{K_2}' of aspartic acid are anomalous in the presence of $MgCl_2$ (but normal with NaCl).

Isoelectric points drop with increase in ionic strength.

(The term "index" signifies the negative logarithm of any constant or variable.)

THE HYDROFLUORIDES OF ORGANIC BASES AND A STUDY OF HYDROFLUORIC ACID

BY J. F. T. BERLINER* AND RAYMOND M. HANN**

The literature of organic chemistry abounds in the description and methods of preparation of organic bases and their derivatives. The hydrochlorides, hydroiodides, hydrobromides, sulfates, oxalates and picrates of a majority of the commoner bases have been prepared, analyzed and their physical properties recorded.

During the investigational work on the quantitative preparation of 5-iodo-2-amino-toluene and some of its more common derivatives¹ the authors prepared the hydrofluoric acid addition compound of the above base. Upon estimation of the nitrogen content of the above salt (Kjeldahl-Gunning-Arnold method) 4.44 per cent of nitrogen was found instead of the 5.52 per cent calculated for a compound $C_8H_8(CH_3)I.NH_2.HF$. This material was prepared three times and recrystallized repeatedly on the supposition that some impurity was affecting the results, but upon reanalysis of these highly purified materials practically the same nitrogen content was found as in the first preparation.

At an earlier date one of the authors had prepared and analyzed some *o*-toluidine hydrofluoride and found that although recrystallized several times, the nitrogen content remained practically constant between the limits 7.40 to 7.47 per cent instead of yielding the 11.02 per cent nitrogen calculated for the compound $C_7H_7(CH_3).NH_2.HF$. At the time this discrepancy was thought to be due to some extraneous cause and no further thought was given to it. This compound and its analysis were recalled to mind when the disparity in the nitrogen content of the iodo-*o*-toluidine was noted.

Upon inspection of the analytical results obtained by the nitrogen analysis of the *o*-toluidine and iodo-*o*-toluidine, it seemed evident that there might be two or three factors acting separately or together, which could be held responsible for the great difference between the amount of nitrogen actually found and the theoretical amount calculated from the general 1:1 base-halogen acid addition product. Possible factors were that the derivative could contain water of crystallization, that a polymer of hydrofluoric acid combined with the base, or that several unpolymerized molecules of the acid combined separately. Should the first factor be true, the nitrogen content of *o*-toluidine hydrofluoride would correspond to a compound containing about 33.15 per cent of water and therefore equivalent to the formula (C_7H_7) .

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¹ Hann and Berliner: *J. Am. Chem. Soc.*, 47, 1709 (1925).

$\text{CH}_3\text{NH}_2\cdot\text{HF})_3\cdot 7\text{H}_2\text{O}$. According to the other latter suppositions, the salt would contain 42.71 per cent of hydrofluoric acid or equivalent to the formula $\text{C}_6\text{H}_4\cdot\text{CH}_3\cdot\text{NH}_2\cdot 4\text{HF}$.

It was noted that upon heating *o*-toluidine hydrofluoride it readily sublimed and upon analyzing the sublimed product it was found to be of the identical composition as before sublimation. A portion of this *o*-toluidine derivative was allowed to stand in a vacuum desiccator over P_2O_5 for eight days and another portion placed in an electric drying oven at 106°C . for 14 hours. These samples, upon analysis, revealed a nitrogen content (7.37 per cent and 7.42 per cent, respectively) corresponding almost exactly with the previous analysis,— 7.40% N.

These results seemed to indicate conclusively that the material did not contain any water of crystallization and that it was probable that four molecules of hydrofluoric acid combined with *o*-toluidine and iodo-*o*-toluidine.

A very careful survey of the available literature revealed the fact that little work had been done upon the reactions of hydrofluoric acids and organic bases. Beilstein² reports aniline hydrofluoride as $\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HF}$, and cites a paper by Beamer and Clark³ published in 1879. These authors during the course of study of common salts of aniline report as follows on aniline hydrofluoride. "Splendid pearl white scales were formed by the mixing of aniline and hydrofluoric acid. The salt is easily soluble in boiling alcohol, however, separating so rapidly on cooling from solution that it stops up the mouth of the funnel through which it is being filtered." No analysis is given or formula presented and it appears as if Beilstein had himself introduced the above formula.

Wallach⁴, a few years later, in discussing the preparation of organic fluorine compounds, indicates the preparation of crystalline aniline hydrofluoride (see p. 260) but gives no analysis or further description.

No other work appeared until 1903, when Hantzsch and Vock⁵ reported on some diazonium hydrofluorides which were water soluble, quite unstable, and were capable of undergoing the general diazonium reactions. They gave meager analytical data and assumed that the compounds formed were of the general formula $\text{R}\cdot\text{N}_2\cdot\text{F}\cdot\text{HF}$, viz., $\text{C}_6\text{H}_2\cdot\text{Br}_3\cdot\text{N}_2\cdot\text{F}\cdot\text{HF}\cdot 2\text{H}_2\text{O}$ and $\text{C}_6\text{H}_4\cdot\text{NO}_2\cdot\text{N}_2\cdot\text{HF}\cdot\text{H}_2\text{O}$.

A few years later Weinland and Lewkowitz⁶ published a paper on hydrofluorides of some anilides and substituted anilines, an extension of Weinland's earlier investigation⁷ upon some double salts of hydrofluoric acid. Somewhat later Weinland with Reischle⁸ reported on some hydrofluorides of weak organic bases. A more manifest discussion of the work of Weinland and his

² Beilstein: "Handbuch der anorganischen Chemie", 3rd Ed., 2, 310.

³ Beamer and Clarke: Ber., 12, 1067 (1879).

⁴ Wallach: Ann., 235, 255 (1886).

⁵ Hantzsch and Vock: Ber., 36, 2059 (1903).

⁶ Weinland and Lewkowitz: Z. anorg. Chem., 45, 39 (1905).

⁷ Ann., 315, 357 (1901); 328, 145, 149 (1903).

⁸ Weinland and Reischle: Ber., 41, 3671 (1908).

collaborators is possible after presentation of our own analytical and experimental results.

Since no further record of hydrofluoric acid derivatives could be found and in view of the unusual results noted with the previously mentioned bases, a study of the compounds of hydrofluoric acid and various types of organic bases was instituted. Derivatives of over twenty-five bases were prepared, carefully purified and analyzed. The analyses of these compounds in every instance indicated the derivative to be of the type B_4HF where "B" represents an aliphatic or aromatic primary, secondary, or tertiary base. Similarly the diamines reacted with hydrofluoric acid to form derivatives of the type $R_2(NH_2)_2(4HF)_2$. Compounds of this general composition were prepared in dilute and concentrated, heated and cooled aqueous, ethereal, and alcoholic solutions of hydrofluoric acid. The results were concordant throughout and indicate that in some manner organic bases add on four molecules of hydrofluoric acid.

Experimental

1. Preparation and Properties.

The general procedure employed in the preparation of the hydrofluoric acid derivatives was to add 0.4 to 0.7 moles (15 to 25 cc.) of pure 48 per cent hydrofluoric acid directly to the base or to an ether or acetone solution containing 0.1 mole of the purified base. The reaction was exothermic, and upon cooling the hydrofluoride separated in nearly quantitative yields. The acid salts are readily recrystallized from hot dilute aqueous solutions of hydrofluoric acid, separating as colorless crystalline compounds. As a rule three recrystallizations were made although analyses indicated that a single recrystallization gave a pure product. With the exception of the dimethyl and diethyl amines, pyridine, quinoline and quinaldine, all the hydrofluorides crystallized well. Even monomethyl aniline and monoethyl aniline whose mineral acid salts are not crystallizable, readily form beautiful crystals of the hydrofluoric acid derivatives.

A rather remarkable property noted was that nearly all the hydrofluorides sublimed unchanged upon heating. Hydrofluorides of metanilic and sulfanilic acids and of *o*-toluidine decomposed. The only hydrofluorides examined which gave a characteristic melting point were *m*-nitraniline (m.p. 207-9°C. cor.), *p*-nitraniline (m.p. 173-4°C. cor.), anthranilic acid (m.p. 217-18°C. cor.) and ethyl aniline (m.p. 170-1°C. cor.).

2. Analytical

(a) Nitrogen

All the hydrofluorides prepared were analyzed for nitrogen by methods of the Association of Official Agricultural Chemists.⁹ These results are presented in Table I and it will be noted with what close agreement our results correspond with those required by the general formula B_4HF .

⁹ "Methods of Analysis", A. O. A. C. 2nd Edition (1925).

TABLE I
Nitrogen Analyses on Hydrofluorides

| Compound | Analysis | | % N found | % N theory B. 4HF |
|-------------------------|-------------------------------------|-----------------------------------------|-----------|----------------------|
| | Weight of sample taken for analysis | Cubic centimeters of N/10 Acid consumed | | |
| Aniline | .1065 | 6.1 | 8.02 | 8.09 |
| o-Toluidine | .1330 | 7.0 | 7.36 | 7.48 |
| m- " | .1030 | 5.5 | 7.48 | 7.48 |
| p- " | .1847 | 9.8 | 7.43 | 7.48 |
| m-Nitraniline | .2152 | 19.6 | 12.76 | 12.84 |
| p- " | .1274 | 11.4 | 12.53 | 12.84 |
| m-Xylidine | .1197 | 6.0 | 7.02 | 6.96 |
| Cymidine | .1052 | 4.6 | 6.12 | 6.11 |
| ψ -Cumidine | .1633 | 7.7 | 6.60 | 6.51 |
| o-Tolidine | .1074 | 5.8 | 7.56 | 7.52 |
| Di-phenylamine | .1336 | 5.4 | 5.66 | 5.62 |
| Tri-phenyl Guanidine | .1006 | 7.6 | 10.58 | 10.44 |
| p-Phenetidine | .1087 | 5.0 | 6.44 | 6.44 |
| o-Anisidine | .1442 | 7.2 | 6.99 | 6.89 |
| p-Nitro-o-Anisidine | .1339 | 10.6 | 11.09 | 11.28 |
| α -Naphthylamine | .1029 | 4.6 | 6.26 | 6.28 |
| β - " | .1304 | 5.8 | 6.23 | 6.28 |
| Iodo-o-Toluidine | .1205 | 3.8 | 4.41 | 4.47 |
| Anthranilic Acid | .1160 | 5.3 | 6.40 | 6.45 |
| Methyl Aniline | .2145 | 11.4 | 7.44 | 7.48 |
| Ethyl Aniline | .1256 | 6.2 | 6.91 | 6.96 |
| Metanilic Acid | .1093 | 4.3 | 5.51 | 5.54 |
| Sulphanilic Acid | .1329 | 5.3 | 5.58 | 5.54 |

(b) Carbon

While the determination of nitrogen content presented a rapid and convenient method of analysis, a more complete analysis was considered essential. Attempts to determine carbon and hydrogen by combustion in the usual manner failed to lead to concordant results. The hydrofluoric acid was apparently not oxidized under the conditions; but passed on into the absorption train and was absorbed, yielding high results for carbon and low results for hydrogen. A second contributing factor to discordant results was traced to reaction of the unoxidized hydrofluoric acid with the combustion tube.

About this time Wilde and Lochte¹⁰ published their work upon a rapid method for the determination of carbon in organic compounds. In the described procedure the compound is burned in the presence of compressed oxygen in a calorimeter containing standard barium hydroxide solution. The carbonate formed is determined by differential titration using phenolphthalein and methyl orange. Several hydrofluorides were successfully

¹⁰ Wilde and Lochte: J. Am. Chem. Soc., 47, 440 (1925).

analyzed by a modification of this procedure and incorporation of Lindner's¹¹ process for the determination of carbonate.¹²

Following combustion in presence of an excess of $\text{Ba}(\text{OH})_2$, the solution was titrated in the cold until colorless to phenolphthalein. The solution was now transferred to a 350 cc. Erlenmeyer flask with a measured excess of .2N hydrochloric acid, a reflux condenser attached and the solution boiled gently for 15 minutes. The excess of hydrochloric acid was now titrated back with $\text{Ba}(\text{OH})_2$ and the volume of acid consumed by the carbonate obtained by difference. This procedure was necessary because barium fluoride reacts acid in water solution, preventing direct titration.

The summary of the analytical results on carbon is given in Table II.

TABLE II
Carbon Analyses on Hydrofluorides

| Hydrofluoride | | Weight sample | Cc. N/5 HCl consumed | Weight C | Found % C | Calculated B.4HF |
|------------------|---|---------------|----------------------|----------|-----------|------------------|
| Aniline | a | .1715 | 59.26 | .07110 | 41.46 | 41.59 |
| | b | .1522 | 52.68 | .06322 | 41.54 | |
| | c | .1155 | 40.20 | .04824 | 41.77 | |
| o-Toluidine | a | .1212 | 45.31 | .05438 | 44.87 | 44.89 |
| | b | .1704 | 63.64 | .07637 | 44.82 | |
| Ethyl aniline | a | .1360 | 53.98 | .06479 | 47.64 | 47.73 |
| | b | .1311 | 51.92 | .06232 | 47.54 | |
| p-Phenetidine | a | .1693 | 62.98 | .07559 | 44.65 | 44.21 |
| | b | .1263 | 46.70 | .05605 | 44.38 | |
| ψ -Cymidine | a | .1164 | 51.58 | .06190 | 53.18 | 52.36 |
| | b | .1394 | 61.80 | .07417 | 53.21 | |

(c) Fluorine

No particular trouble was experienced in the determination of the fluorine content of these compounds, since the attached hydrofluoric acid may be removed by solution in strong alkali. The sample (.2 gm.) was treated with 3 cc. of 4N KOH, water added to a volume of 20 cc., the solution adjusted to methyl red neutrality with dilute HCl, 5 cc. of N Na_2CO_3 added and then heated to boiling. Ten cc. of 20 per cent CaCl_2 solution was now added and the solution allowed to digest on the steam bath for 1/4 hour. This was cooled to 14°C., 3 to 5 cc. of concentrated acetic acid added and after allowing it to cool to about 15-20°C., filtered through a weighed Gooch crucible, washed sparingly with cold dilute acetic acid, dried and weighed. The filtrate was measured and the loss for solubility of CaF_2 in filtrate corrected for (.0016 gms. per 100 cc.).

The results are tabulated in Table III.

¹¹ Lindner: Ber., 55, 2025 (1922).

¹² We are indebted to Dr. H. L. Lochte and Mr. G. Decherd, of the University of Texas for devising the method and performing the analyses on carbon.

TABLE III
Fluorine Analyses on Hydrofluorides

| Hydrofluoride | | Weight Sample | Weight CaF ₂ | Found | % F Calculated B. ₄ HF |
|------------------------|---|---------------|-------------------------|-------|--------------------------------------|
| Aniline | a | .2000 | .1804 | 43.90 | 43.91 |
| | b | | .1801 | 43.83 | |
| Cymidine | a | | .1362 | 33.15 | 33.16 |
| | b | | .1362 | 33.15 | |
| p-Phenetidine | a | | .1436 | 34.95 | 35.00 |
| | b | | .1432 | 34.85 | |
| Methyl aniline | a | | .1670 | 40.64 | 40.62 |
| | b | | .1666 | 40.55 | |
| m-Nitraniline | a | | .1431 | 34.83 | 34.85 |
| | b | | .1429 | 34.78 | |
| o-Tolidine | a | | .1677 | 40.81 | 40.84 |
| | b | | .1675 | 40.76 | |
| β -Naphthylamine | a | | .1397 | 34.00 | 34.06 |
| | b | | .1396 | 33.98 | |

From these data it is apparent that the nitrogen, carbon and fluorine contents of a variety of hydrofluorides agree remarkably well with a general formula B.₄HF. It is noteworthy that o-tolidine, a diamine, adds eight moles of HF per mole of base.

(d) Titration studies

Compounds of strong acids with weak bases are normally titratable with a strong base. It was observed that the addition compounds under discussion dissolved in warm water to yield acid solutions, presumably due to a partial hydrolysis of the compound.

That some hydrolysis actually takes place is quite apparent in the instance of the nitraniline hydrofluorides which on contact with water are immediately transformed from colorless to yellow crystals, yielding yellow solutions.

An attempt was made to titrate solutions containing known amounts of these hydrofluoride salts with various strengths of standard sodium hydroxide solutions and using indicators with transformations in several ranges of hydrogen ion concentration. All attempts led to the general result that when an indicator having a range above a pH of 6 was employed only three-fourths of the combined acid (on the assumption of 4HF) could be titrated.

A great number of trials were made varying the several conditions such as temperature, concentration of salt and alkali, solvent, addition of various neutral salts, and the use of indicators corresponding to several ranges of acidity. The results of all these experiments were analogous—only *three-fourths* of the hydrofluoric acid could be accounted for.

With indicators whose transformations corresponded to ranges higher than a pH of 9, the amount of acid that appeared titratable increased, but the results were extremely erratic. Determinations varied from 75 per cent

to 85 per cent and in one instance as high as 92 per cent of the calculated amount of hydrofluoric acid present in the compound. In these higher ranges the end points of the titrations were never sharp and in most cases extended over unusually wide ranges.

It was thought that this extraordinary behavior was due to some peculiar property of hydrofluoric acid and a search was made for reports of previous titrations of this acid. The only study that was found that dealt specifically with this subject was by Haga and Osaka¹³ who titrated various strengths of

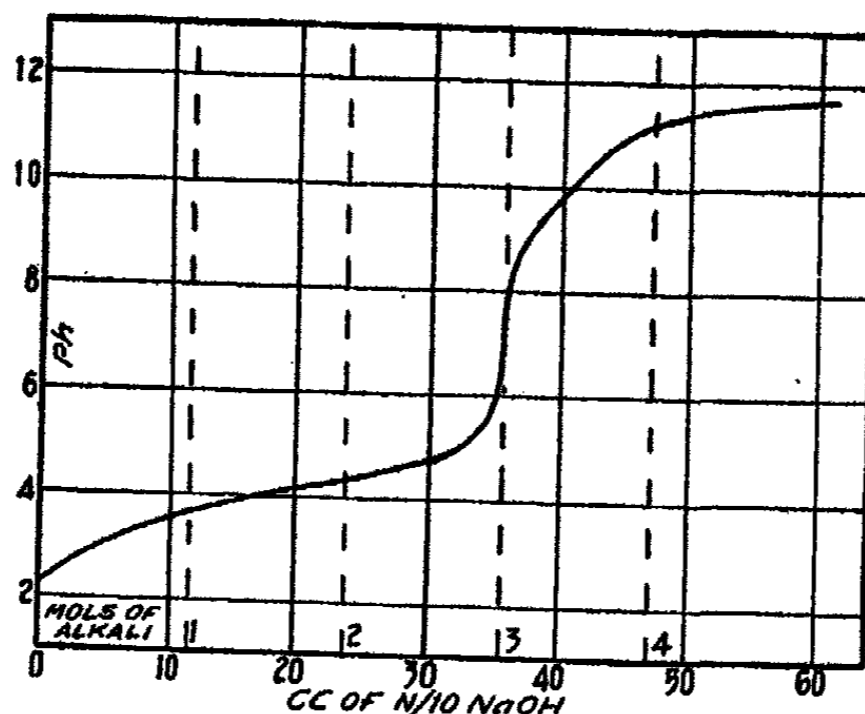


FIG. 1

Typical electrometric titration curve for the organic base hydrofluorides.
Dashed vertical lines represent moles of alkali per mole of hydrofluorides.

hydrofluoric acid in aqueous solution with alkali using a number of indicators. In the use of litmus as an indicator the results obtained caused the authors to suggest that the molecule of hydrofluoric acid might be H_2F_2 , H_3F_3 or H_4F_4 . The analysis of the neutralized solution indicated a composition of K_3HF_4 . However, their results show that in general all the hydrofluoric acid present can be readily and completely titrated by the indicator method and that a number of indicators may be employed, (phenolphthalein was considered the most satisfactory).

From our previous results and the above contribution it seemed apparent the peculiar behavior noted was due primarily to the types of compound with which we were dealing. These data indicate that one of the hydrogen fluoride molecules of the $(HF)_4$ complex is in combination in a manner differing from that of the other three.

Since coordinate results could not be obtained by the indicator method of titration, a series of electrometric titrations were made with the hope of being able to interpret the above data and gain an insight into the mechanism of the complete neutralization of these compounds.

¹³ Haga and Osaka: *J. Chem. Soc.*, 67, 251-255 (1895).

These titrations were made using a normal calomel cell and the Hildebrand type of hydrogen electrode. The volume of the solution was approximately 100 cc. at the start and the concentration of the salt about .01 N.

Several of the salts were very carefully titrated electrometrically, and the results of the electromotive force measurements converted into their equivalent pH values and plotted. It was of interest to note that all the compounds thus titrated (9) yielded analogous types of neutralization curves. A typical curve is represented in Fig. 1.

This curve, representing the titration of 0.1966 grams (0.001136 moles) of aniline hydrofluoride with 0.1 N NaOH, has several interesting and noteworthy features. The acid nature of the solution, undoubtedly due to hydrolysis, is evidenced by the high hydrogen ion concentration (low pH) of the initial solution. As the alkali is added neutralization takes place smoothly until an equivalent of three moles of the alkali have been added or three-fourths of the available hydrofluoric acid accounted for.

As neutralization proceeds from this point, a very peculiar condition appears. Instead of the curve rising rapidly to a value of pH of about 10.0 to 11.0 (within the range of 0.1% excess alkali) as is the case in the course of a normal type of neutralization, there is a sharp slowing up in the rate of the decrease of the hydrogen ion concentration in a range represented by about pH 7.5-8.0. From this point the addition of alkali is in a nearly linear relation to the increase in the value of pH. The equivalent of approximately one more mole of alkali, making a total of four moles, must be added to bring the curve to the range attained by the addition of 0.1% excess alkali in a normal type of neutralization under the above conditions. Further addition of alkali causes the curve to act in the normal manner.

From an inspection of this curve which is typical for all the compounds titrated electrometrically it will be immediately apparent why difficulties were encountered in titrations by the indicator method. It may be noted at once that for indicators whose point of equilibrium in the color transformation range represented by a pH value in the proximity of 8 will give an apparent end point at 75% of the total available acid while those indicators having transformations at lower hydrogen ion concentrations will show a proportionately higher acid content. The very wide range of neutralization between the alkali equivalent of three and four moles shows that the end point of any titration that lies within this range will be extremely difficult to distinguish with an accuracy closer than 10 to 20% of the total alkali necessary to cause complete neutralization.

It is, therefore, quite apparent that the base hydrofluorides cannot be completely titrated satisfactorily by means of the indicator method. However, by the use of indicators of the proper range it would be possible to titrate exactly 75% of the total acid present in the compounds. In Table IV some of the numerical results for the electrometric titrations of some of the compounds are given.

TABLE IV
Typical Electrometric Titration Results

| Aniline hydrofluoride 0.1966 g. in 100 cc. | | Cymidine hydrofluoride 0.1689 g. in 100 cc. | | p-Phenetidine hydrofluoride 0.1156 g. in 100 cc. | |
|--------------------------------------------------|-------|---------------------------------------------------|-------|--------------------------------------------------------|-------|
| cc N/10 NaOH | Ph | cc N/10 NaOH | Ph | cc N/10 NaOH | Ph |
| 0 | 2.30 | 0 | 2.73 | 0 | 2.63 |
| 5 | 3.07 | 4 | 3.47 | 2 | 3.19 |
| 10 | 3.52 | 8 | 3.84 | 4 | 3.60 |
| 15 | 3.89 | 12 | 4.17 | 6 | 3.92 |
| 20 | 4.17 | 16 | 4.42 | 8 | 4.19 |
| 25 | 4.42 | 20 | 4.76 | 10 | 4.39 |
| 30 | 4.74 | 21 | 4.93 | 12 | 4.68 |
| 32 | 4.90 | 22 | 5.27 | 13 | 4.92 |
| 34 | 5.30 | 22.5 | 5.73 | 14 | 5.22 |
| 35 | 5.93 | 23 | 7.85 | 14.5 | 5.42 |
| 35.5 | 7.22 | 23.5 | 8.70 | 15 | 5.66 |
| 36 | 8.16 | 24 | 9.07 | 15.5 | 5.98 |
| 36.5 | 8.54 | 24.5 | 9.34 | 16 | 6.76 |
| 37 | 8.78 | 25 | 9.58 | 16.5 | 8.54 |
| 37.5 | 9.00 | 25.5 | 9.80 | 17 | 9.10 |
| 38 | 9.17 | 26 | 10.00 | 17.5 | 9.43 |
| 39 | 9.46 | 26.5 | 10.23 | 18 | 9.71 |
| 40 | 9.73 | 27 | 10.42 | 18.5 | 9.97 |
| 41 | 10.01 | 27.5 | 10.58 | 19 | 10.24 |
| 42 | 10.31 | 28 | 10.70 | 19.5 | 10.49 |
| 43 | 10.59 | 28.5 | 10.85 | 20 | 10.71 |
| 44 | 10.80 | 29 | 10.95 | 20.5 | 10.86 |
| 45 | 10.95 | 29.5 | 11.03 | 21 | 10.98 |
| 46 | 11.07 | 30 | 11.10 | 21.5 | 11.08 |
| 47 | 11.16 | 31 | 11.20 | 22 | 11.15 |
| 48 | 11.24 | 32 | 11.30 | 23 | 11.27 |
| 50 | 11.36 | 36 | 11.55 | 24 | 11.36 |
| 55 | 11.54 | 40 | 11.66 | 30 | 11.67 |
| 60 | 11.68 | 50 | 11.84 | 45 | 11.96 |

A consideration of the reasons for this remarkable behavior is beyond the present scope of this paper. It is incumbent, however, to prove that the effect is due to a peculiar property of these addition compounds only, and not to some extraneous factor.

The factor that might be considered to be the most probable cause of any such deviation from the normal is that of the hydrofluoric acid, another consideration is that of the mechanism of neutralization of organic base salts such as the hydrochlorides.

In view of these possibilities, a series of electrometric titrations were made on aqueous solutions of hydrofluoric acid of various strengths (0.001, 0.01

and 0.1 N) and on aqueous solutions of aniline hydrochloride. Both of these materials give results strictly analogous to the normal strong acid-base neutralization. In Fig. 2 are represented the superimposed neutralization curves of aniline hydrofluoride and hydrofluoric acid (0.1N). The curve for aniline hydrochloride has been omitted since it so closely parallels that of the hydrofluoric acid.

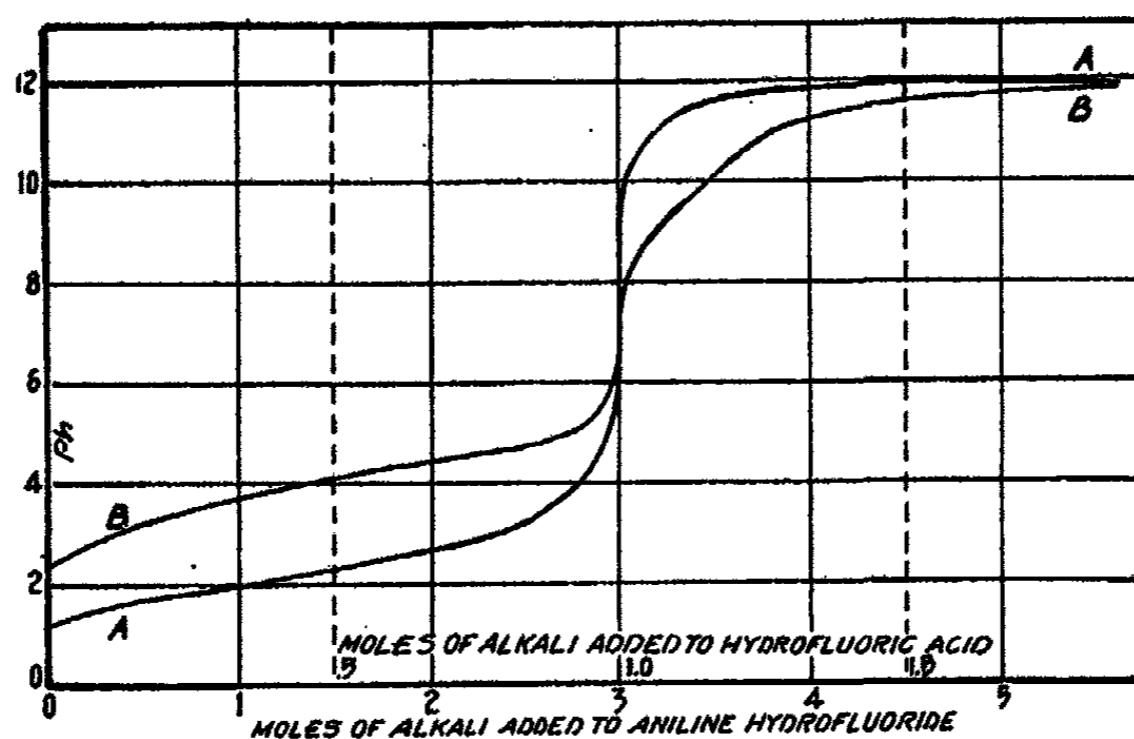


FIG. 2
Comparison of electrometric titration curves of hydrofluoric acid (A)
and aniline hydrofluoride (B).

Consequently, it may be stated that without doubt the peculiar characteristics noted in the mechanism of neutralization of the hydrofluorides of the organic bases are an intrinsic and individual property of these compounds, and that the separate compound constituents of these salts behave in the normal manner.

In consideration of the above contentions and experimental results, it is postulated that in these organic base hydrofluorides there are present four molecules of hydrofluoric acid, three of which are bound to the molecule in a manner distinctly differing from the fourth. The constitutional relations of three molecules of the acid to the base are identical. In solution, doubtlessly, these three molecules are hydrolyzed from the base simultaneously and to the same extent, and the neutralization in relation to these proceeds in a normal manner. However, at the very point of the neutralization of these three molecules of hydrofluoric acid there is left in solution the base hydrofluoride with the one molecule of hydrofluoric acid that is bound in an entirely different manner to the base than the other three molecules of acid. From this point on, the course of the neutralization is distinctly not normal, and it is not within the domains of this discussion to attempt an explanation of the actual mechanism of the neutralization of this last molecule of hydrofluoric acid.

That the first three molecules of hydrofluoric acid attached to the organic base are not individually neutralized or rather hydrolyzed from the base is evidenced by the smooth, unbroken portion of the electrometric titration curve up to the utilization of about 75% of the available acid.

A consideration of the possible structural constitution of these compounds based on the above results will be found in a subsequent portion of this discussion.

Discussion of the Work of Weinland and Lewkowitz⁶ and of Weinland and Reischle⁸

In entering upon a discussion of the work of these authors, it is our intention to merely point out possible sources of agreement between their data and our own.

These authors investigated the action of hydrofluoric acid on aromatic anilides and amines and described in all twenty-four compounds, of which about half are of the amine type. It is with this latter group that we are at present concerned.

They described the following compounds: Aniline monofluorhydrate ($C_6H_5NH_2 \cdot HF \cdot 1.5H_2O$), aniline difluorhydrate ($C_6H_5NH_2 \cdot 2HF$), aniline trifluorhydrate ($C_6H_5NH_2 \cdot 3HF \cdot 1.5H_2O$), p-amidophenol trifluorhydrate ($C_6H_4(OH)NH_2 \cdot 3HF \cdot 1.5H_2O$), p-amidophenetol difluorhydrate ($C_6H_4(OC_2H_5)NH_2 \cdot 2HF$), p-amido-benzoic acid difluorhydrate ($C_6H_4(COOH)NH_2 \cdot 2HF$), p-bromaniline tri-fluorhydrate ($C_6H_4BrNH_2 \cdot 3HF \cdot H_2O$), and o-, m-, and p-nitraniline tri-fluorhydrates ($C_6H_4(NO_2)NH_2 \cdot 3HF \cdot H_2O$), triphenyl amine monohydrofluoride ($(C_6H_5)_3N \cdot HF$) and diphenyl amine, di- and trihydrofluorides ($(C_6H_5)_2NH \cdot 2HF$ and $(C_6H_5)_2NH \cdot 3HF$).

Since such diversity of combination was in sharp contrast to the uniformity which we had experienced, an examination of the analytical and experimental data of Weinland and Lewkowitz was undertaken. This survey revealed the fact that in a number of instances, the formulae assigned to the compounds were based upon titration values with tenth-normal alkali. It has been demonstrated that such titration allows the estimation of but about three-fourths the combined hydrofluoric acid. Formulae based on the assumption of total titration would therefore be incorrect.

Another source of difference between our compounds and some of those of Weinland and his collaborators is that in all cases our derivatives were prepared in the presence of an excess of acid while this was not the case with several of the preparations described by the above authors.

For one of the compounds of the amine type, complete analytical results on carbon, hydrogen, and fluorine are given. No indication is supplied regarding the procedure employed, and from a consideration of the difficulties enumerated in a previous section regarding the estimation of carbon and hydrogen in these compounds, we would prefer not to discuss this compound.

Four of the remaining compounds were not prepared in an excess of acid, namely aniline mono- and dihydrofluorides, triphenylamine monohydrofluoride and diphenylamine dihydrofluoride. In the instance of two other

derivatives no indication is given of the amount of acid used, but evidently there was not an excess of acid (p-amido-phenetol dihydrofluoride and p-amido benzoic acid dihydrofluoride).

Eliminating these hydrofluoride derivatives from further consideration, but six compounds remain to be discussed. These will be separately considered.

1. Aniline hydrofluoride.—The empirical formula for this compound is given as $C_6H_5NH_2 \cdot 3HF \cdot \frac{1}{2}H_2O$, based on four titrations with N/10 KOH which averaged, show a hydrofluoric content of 36.6%. Assuming that but three-fourths of the acid was titrated and the empirical formula was that of the compound described in this paper, viz. $C_6H_5NH_2(HF)_4$, the result theoretically would be 34.7% which is reasonably close to the above result. There is no analytical evidence given which could possibly allow the assumption of the constitution of the compound to be as presented.

2. p-Bromaniline hydrofluoride.—The empirical formula proposed for this compound is $C_6H_4Br \cdot NH_2 \cdot 3HF \cdot H_2O$, and as in the previous case, the only analytical data presented is that of titration with N/10 KOH. It is immediately noted that the molecular weight corresponding to the above would be almost identical with that corresponding to $C_6H_4Br \cdot NH_2 \cdot 4HF$. Therefore, assuming that but three-fourths of the total acid was titrated, the latter formula may be considered the more correct.

3. (a, b and c) o-, m-, and p-nitroaniline hydrofluorides.—The empirical formulae presented for these compounds are the same, and correspond to $C_6H_4NO_2 \cdot NH_2 \cdot 3HF \cdot H_2O$. This is likewise based on acidimetric titrations. In the case of the ortho isomer, a nitrogen analysis is included which agrees very well with our result (W. & L. 12.8%, our value 12.76%). As in the instance of the p-bromaniline hydrofluoride, the molecular weight of these compounds is almost identical with that of $C_6H_4NO_2 \cdot NH_2(HF)_4$, and since the nitrogen analysis corresponds with this formula as well as for that given and the formula proposed by Weinland, et al., is based on the incorrect assumption that all the hydrofluoric acid was titrated, it is contended that the compounds he was describing are of the type $C_6H_4NO_2 \cdot NH_2(HF)_4$.

4. Diphenyl amine hydrofluoride.—The empirical formula proposed for this compound is $(C_6H_5)_2NH \cdot 3HF$ based on titration data and a nitrogen determination. The nitrogen result lies practically midway between the calculated value for the above compound and that for $(C_6H_5)_2NH \cdot 4HF$. Since the titration values represent but three-fourths of the total acid, the proposed composition is considered erroneous. The compound has the composition represented by the tetrahydrofluoride.

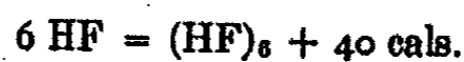
From this brief summation it appears evident that the analytical data presented by Weinland and his coworkers to establish the empirical composition of the hydrofluorides of the various amines are in agreement with our results and support the contention that when an excess of hydrofluoric acid acts on any amine, a compound of the general type $R \cdot NH_2 \cdot (HF)_4$ is formed.

It can be shown by a recalculation of the data that the analytical results on the aniline hydrofluoride are also in concordance with this precept. However, since we have not prepared any of this type of compound, we do not desire to enter into a discussion of this phase at the present.

The Abnormality of Hydrofluoric Acid

The present conflicting evidence of the nature of hydrofluoric acid and the limited knowledge regarding its reactions make any discussion of the constitution of the compounds of the type considered in this paper, rather uncertain.

Much work has been done on anhydrous hydrofluoric acid, both in the gaseous and liquid states. It has been shown through vapor pressure measurements that the vapor has a molecular weight of 37.32 at 30.5°C. indicative of a molecular formula $(\text{HF})_2$ ¹⁴. Simons and Hildebrand¹⁵ have shown the molecular weight of the vapor to be 39.74 at 305.1°K (40 at 305°K) and from data on the vapor pressure of highly purified anhydrous hydrofluoric acid they calculated that at any temperature it may consist of an equilibrium mixture of the isomers HF and $(\text{HF})_6$. They present evidence to indicate that the polymerization is exothermic and may be represented as



Von Wartenberg and Fitzner¹⁶ have recently correlated and made a study of the thermochemical data on fluorine using the above assumption of Simons and Hildebrand in order to correct for the degree of polymerization of hydrofluoric acid in the calculation of the heat of solution and other derived values.

There has been quite some discussion upon the molecular complexity of hydrofluoric acid, as evidenced by its abnormal boiling point, by Forcrand¹⁷ and by Berthoud^{18,19}. The former is of the opinion that the abnormal boiling point of hydrofluoric acid as well as that of water and of ammonia are not due to molecular association but to the high heat of formation of these compounds due to a di-symmetry of their molecules. Berthoud, however, does not accept this view and shows that the abnormally high points of ebullition are readily accounted for by the polarity of these substances and that molecular asymmetry is not sufficient to cause such high boiling points.

Recently Kolossowsky²⁰ has pointed out an error in Simons' calculations of the heat of vaporization, thereby showing that it is in agreement with previous determinations.

From the extrapolated vapor density data of Thorpe and Hambly and applying Trouton's rule according to the principle of DeHeen, he arrives at the remarkable conclusion that hydrofluoric acid boils as a normal, non-

¹⁴ Mallet: *Am. Chem. J.*, 3, 189 (1881).

¹⁵ Simons and Hildebrand: *J. Am. Chem. Soc.*, 46, 2187 (1924).

¹⁶ Von Wartenberg and Fitzner: *Z. anorg. allgem. Chem.*, 151, 313 (1926).

¹⁷ Forcrand: *J. Chim. phys.*, 15, 517 (1917).

¹⁸ Berthoud: *J. Chim. phys.*, 15, 3 (1917).

¹⁹ Berthoud: *J. Chim. phys.*, 16, 245 (1918).

²⁰ Kolossowsky: *Bull.*, (6), 51-52, 422-28 (1927).

associated liquid, i.e. its degree of association at its boiling point and in the saturated vapor at the same temperature is the same. This association is shown to correspond to the empirical formula H_3F_3 .

Henglein²¹ in a study of the physical properties and molecular structure of the halogens and their compounds finds that all of these substances, with the exception of hydrofluoric acid, are in very fine agreement with the rule proposed by Biltz²², i.e., that the physical properties (melting point, optical properties, thermal relations, etc.) of the halogens and their compounds are in linear relationship to the molecular volume. However, hydrofluoric acid was so abnormally different that it was completely excluded.

While much study has been devoted to the anhydrous acid, relatively slight consideration has been given to the molecular complexity of hydrofluoric acid in aqueous and other solutions.

Some work has been done on the conductivity and activity of hydrofluoric acid in aqueous solution. Wynne-Jones and Huddleston²³ found that for concentrations up to 0.4 N the activities of the hydrogen ions were in concordance with the calculated values while above this concentration a marked abnormal deviation occurred. Kreman and Decolle²⁴ from conductivity data rendered an opinion that hydrofluoric acid is dibasic and that fluorine is divalent, while Walden²⁵ also measured the conductivity relations and on the contrary postulated its monobasicity.

By studying the change of conductivity of hydrofluoric acid solutions during neutralization Pellini and Pegoraro²⁶ found that a minimum in the specific conductivity occurred at 0.5 moles of alkali and contended that this proved the basicity of the acid. However, Bruni²⁷ has shown that the results of Pellini and Pegoraro were merely fortuitous, for their results would have been different if any other concentration of acid had been investigated. Bruni shows that the minimum of the specific conductivity curve varies with the concentration.

However, there seems to be more or less complete agreement among investigators that in aqueous solution the acid exists partly as the HF_2 ion. Pick²⁸ assumed that HF_2 existed in solution while there was no appreciable amount of H_2F_2 present and the complex ion was formed by the dissociation of mono-basic hydrofluoric acid, and the reaction of the fluorine ion with undissociated mono-basic hydrofluoric acid. He calculated the equilibrium constant of this reaction ($HF + F = HF_2$) to be 5.5 and also pointed out that the formation of the complex ion was independent of the acid concen-

²¹ Henglein: *Z. anorg. allgem. Chem.*, **118**, 165 (1921).

²² Biltz: *Z. anorg. allgem. Chem.*, **115**, 241 (1921).

²³ Wynne-Jones and Huddleston: *J. Chem. Soc.*, **125**, 1031 (1924).

²⁴ Kreman and Decolle: *Monatsheft*, **28**, 917 (1907).

²⁵ Walden: *Z. physik. Chem.*, **2**, 58 (1888).

²⁶ Pellini and Pegoraro: *Atti Accad. Lincei*, **16 II**, 273-279 (1907); also *Z. Elektrochemie*, **13**, 621-22 (1907).

²⁷ Bruni: *Z. physik. Chem.*, **69**, 69-74 (1909).

²⁸ Pick: *Nernst Festschrift*, 360-73 (1912).

tration. Davies and Huddleston²⁹ confirmed the existence of this complex ion between the concentrations of 0.16N and 2.3N and calculated the equilibrium constant to be 4.7. Further Anthony and Huddleston³⁰ have ascertained by freezing point methods that no appreciable amount of H_2F_2 exists in solution.

A very good discussion of the general physical properties of aqueous solutions of hydrofluoric acid will be found in the new edition of Gmelin's "Handbuch der anorganischen Chemie" (No. 5, 8th Edition, 1926).

Pick's contribution contains an excellent discussion and summary of the knowledge of the molecular composition and ionization of aqueous solutions of hydrofluoric acid.

In the instance of the compounds with organic bases which we have described, it appears practically impossible to explain the observed phenomena by application of the above briefly outlined investigations. At present, attention to these data merely emphasizes the peculiar and abnormal behavior of hydrofluoric acid.

In proceeding to a survey of the general reactions of this acid, it may be noted that usually when a monatomic fluoride is allowed to crystallize from an excess of hydrofluoric acid, an acid salt is obtained. In a surprisingly large number of instances the acid compounds may be considered as salts of the hypothetical quadribasic hydrofluoric molecule H_4F_4 . Many double salts may also be referred to as derivatives of a parent substance H_4F_4 and listed below are empirical formulae of numerous types of compounds which may be so considered.

$NaF \cdot 3HF^{31}$; $KF \cdot 3HF^{31}$; $RbF \cdot 3HF^{32}$; $LiF \cdot 3HF^{33}$; $MgF_2 \cdot 2NaF^{34}$; $MgF_2 \cdot 2KF^{35}$; $ZnF_2 \cdot 2KF^{36,37}$; $BeF_2 \cdot 2NH_4F^{38}$; $BeF_2 \cdot 2NaF^{38}$; and $BeF_2 \cdot 2KF^{38,39}$.

Poulenc⁴⁰ has prepared a series of double salts of nickel and cobalt with alkali fluorides of general type $NiF_2 \cdot 2NH_4F$; $CoF_2 \cdot 2NaF$, as well as a series containing MnF_2 in place of the alkali fluoride such as $CoF_2 \cdot MnF_2$. Weber⁴¹ has described a similar series containing ferrous fluoride, i.e., $FeF_2 \cdot 2M'F$. A rather detailed compilation of double salts of hydrofluoric acid has been made by Bartezko⁴² and also by Wells⁴³. In their papers are listed many

²⁹ Davies and Huddleston: *J. Chem. Soc.*, 125, 260 (1924).

³⁰ Anthony and Huddleston: *J. Chem. Soc.*, 127, 1122 (1925).

³¹ de Forcrand: *Z. anorg. Chem.*, 28, 384 (1903); Guntz: *Bull.*, (3) 13, 114 (1895); Moissan: *Compt. rend.*, 106, 547 (1881); *Ann. Chim. Phys.*, (6) 3, 5 (1884).

³² Eggelin and Meyers: *Z. anorg. Chem.*, 46, 174 (1905).

³³ Chabrie: *Compt. rend.*, 132, 680 (1901).

³⁴ Netto: *Z. angew. Chem.*, 4, 45 (1890).

³⁵ Duboin: *Compt. rend.*, 56, 848 (1863).

³⁶ Wagner and von Helmholtz: *Ber.*, 19, 896 (1886).

³⁷ Berzelius: *Pogg. Ann.*, 1, 22, 26 (1824).

³⁸ de Marignac: *Arch. Sci. Genève*, (4) 30, 45 (1873).

³⁹ Gay Lussac and Thénard: "Recherches physico-chimiques" (1811); Berzelius: *Pogg. Ann.*, 8, 187 (1826); von Awdejef: 56, 101 (1842).

⁴⁰ Poulenc: *Ann. Chim. Phys.*, (7) 2, 47 (1894).

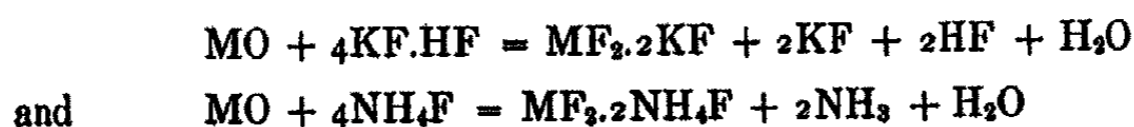
⁴¹ Weber: *J. prakt. Chem.*, 90, 212 (1863).

⁴² Bartezko: "Uber Doppelfluoride" (1909).

⁴³ Wells: *Am. Chem. J.*, 26, 389 (1901).

derivatives which, empirically at least, may be considered as derived from a hypothetical acid H_4F_4 . The alkali metals, silver and cuprous copper form salts KM'_2F_4 where M' represents any univalent basic substance. Divalent metals yield compounds such as $MgM''F_4$ while trivalent metals produce double salts, an example of which is $SbM'F_4$. Marked variation in composition may occur even in these major divisions to form salts such as $K_2M'_2F_4$, $K_2M'F_4$, MgM'_2F_4 , etc. Tetravalent and quinquevalent salts may be considered as derived from H_4F_4 since they form compounds ZrM'_4F_8 and TaM'_5F_{10} . Berzelius³⁷ describes $ZnF_2 \cdot 2AlF_3$ ($ZnAl_2F_8$) and Branner⁴⁴ prepared $PbF_4 \cdot 3KF \cdot HF$ ($HPb''''K_3F_8$).

Bartzeko mentions oxide salts which he formulates as $(AsO).M.F_4$, $(VO).M_2.F_4$ and $(UO).M_2.F_4$. Tellurium salts of this type have been investigated by Metzner⁴⁵ and also by Prideaux and Millot⁴⁶. Little work has been accomplished upon metallic organo fluorides. Krause⁴⁷ has, however, prepared a number of alkyl tin double fluorides similar to $(C_2H_5)_2SnF_2 \cdot 2KF$. Of possible interest in connection with salts of this type are the general reactions:



advanced by Ruff⁴⁸ in an extensive treatise on the chemistry of fluorine.

It has been mentioned that in every instance the compounds described in this paper were recrystallized in the presence of an excess of hydrofluoric acid. It is quite possible that an organic hydrofluoride of lower acid content than four moles might be obtained in the presence of an excess of the amine. However, the present evidence would strongly indicate that an excess of acid being present insures an acid-base combination containing four moles of acid for every amino group present. There seems to be a striking analogy between these compounds and inorganic compounds resembling $KF \cdot 3HF$, which are prepared in a similar manner. That double salts should show a fairly strong tendency to form what may be conceived to be derivatives of the hypothetical acid H_4F_4 also seems significant. There are of course many double salts of the metals whose empirical formulae do not fall into line, but there is in general a decided analogy to be found between a majority of double fluoride salts and the organic compounds we are discussing.

The usual stability of the base hydrofluorides is paralleled by the behavior of inorganic fluorides, several of which are more stable as acid fluorides than as normal fluorides. The earliest observations of this curious phenomenon were

⁴⁴ Branner: *Z. anorg. Chem.*, 7, 1 (1894).

⁴⁵ Metzner: *Ann. Chim. Phys.*, (7) 15, 203 (1898).

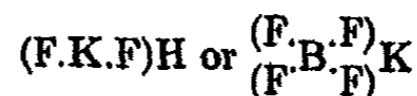
⁴⁶ Prideaux and Millot: *J. Chem. Soc.*, 129, 520 (1926).

⁴⁷ Krause: *Ber.*, 51, 1447 (1918).

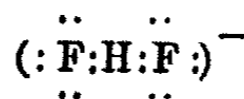
⁴⁸ Ruff: "Die Chemie des Fluors", 17 (1920); Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", 2, 129-141, 512-521 (1922); Abegg and Auerbach: "Handbuch der anorganischen Chemie", 4 II (1913); Gmelin's "Handbuch der anorganischen Chemie", 8th Ed., No. 5 (1926).

made by Wiegleb⁴⁹. Berzelius⁵⁰ and Rose⁵¹ made corresponding observations on the same salt, ammonium fluoride, and found that in hot aqueous solution ammonia is evolved and ammonium acid fluoride results. Even in moist air solid ammonium fluoride was transformed upon standing into the acid salt.

There has been some discussion relative to the valence of fluorine and the structure of its compounds, but no satisfactory or even adaptable hypothesis has as yet been advanced. Werner⁵² assumed that in double fluorides the halogen atoms are united to the central atom or group so that the group acts as an acid anhydride such as



in which the halogen atoms act as intermediate or connecting links between two elementary atoms or groups. Pauling and Hendricks⁵³ in their work on the structure of azides and cyanides by means of X-rays, discuss the possible configuration of hydrofluoric acid and its derivatives and remark that the acid fluoride ion $(HF_2)^-$ may, because of the small charge on the proton as compared with the other kernels, possess a unique electronic arrangement. It is generally believed that in the acid fluoride ion the proton is sharing only two electron pairs with other nuclei. The structure of the ion may be represented thus:



The Electronic Structure of Organic Base Hydrofluorides

The above section is a very brief résumé of the state of knowledge in regard to the structure of hydrofluoric acid derivatives. In all this mass of data there seems to be no direct fact or hypothesis that may be utilized to assist in an explanation of the phenomena of the hydrofluoric acid salts of the organic bases. Yet throughout the presented data there may be discerned a relationship between the inorganic and the organic derivatives. There exists a strong tendency for hydrofluoric acid or inorganic fluorides to become attached to other inorganic fluorides and to form quite stable derivatives. Quite often these compounds contain four atoms of fluorine to the molecule. In the acid fluorides the tendency is to form tri-hydrofluoric acid salts, viz. KF_3HF , when an excess of acid is employed. The latter property is directly analogous to the mode of formation of the organic compounds described in this paper. In every case these were prepared in the presence of an excess of hydrofluoric acid. Another analogy is the fact that, as aforementioned, in the organic hydrofluorides one of the acid groups appears to be

⁴⁹ Wiegleb: Creel's "Die neuesten Entdeckungen in der Chemie", 1, 13 (1781).

⁵⁰ Berzelius: "Lehrbuch der Chemie", 3, 282 (1836).

⁵¹ Rose: Pogg. Ann., 108, 19 (1859).

⁵² Werner: "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 68 (1905).

⁵³ Pauling and Hendricks: J. Am. Chem. Soc., 47, 2904 (1925); 48, 643 (1926).

attached to the base in a manner differing in some respect from the accompanying other three. There may exist an interpretation of these results in the application of principles of molecular structure that have been developed by the studies of Lewis, Thompson and others.

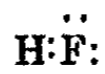
Fluorine, in common with other halogens, may be considered capable of possessing several valences, and as a matter of fact, its most common valence is at present unknown. We may at present assume the existence of the same valences as exhibited by the other halogens. Electronically, fluorine consists of the helium nucleus surrounded by seven orbital electrons. The tendency of such a configuration is to capture an additional electron in order to complete the octet shell. For this reason one would anticipate a valence of one.

Many of the reactions of fluorine and its compounds are quite complex and difficult to explain on the basis of a rigidly univalent element. Even hydrogen is under certain conditions conceived to be divalent and in fact this circumstance may actually exist in hydrofluoric acid. This idea was suggested by Huggins⁵⁴ and was also advanced by Latimer and Rodebush⁵⁵. It is interesting to note in this connection that liquids which are highly associated, and possess the high dielectric constant and ionizing power which apparently accompany this association, are substances containing the type of structure postulated for hydrofluoric acid. This idea of the bivalent hydrogen offers a rather clear conception of the association of such molecules as water, hydrogen peroxide, hydrocyanic acid, ammonia and hydrofluoric acid.

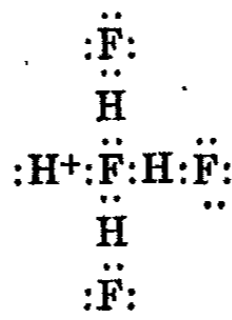
Pauling and Hendricks⁵³, as well as several other investigators, have considered the electronic structure of the hydrofluoric acid ion to be $(\ddot{\text{F}}:\text{H}:\ddot{\text{F}})^-$

where the hydrogen is considered to share four electrons with the fluorine atoms. It may be argued from this that fluorine has the power to cause hydrogen to share this number of electrons when they are in combination. In other words, the hydrogen is rendered strongly negative.

Now if one considers the molecule of hydrofluoric acid as normally represented,



and assumes that through some agency it has been rendered relatively more positive than in the free condition, there would be a tendency for other molecules of hydrofluoric acid, through the negatively charged hydrogen atom, to attach themselves to this molecule in the manner represented below:



⁵⁴ Huggins: *Science*, 40, 679 (1922).

⁵⁵ Latimer and Rodebush: *J. Am. Chem. Soc.*, 42, 1419 (1920).

This type of structure is possible since even the octet does not necessarily have to be considered completely saturated, for though it cannot receive any more electrons, its own electrons may be shared in such a manner as to fill the shells in other atoms, thus completing their octets. As Thomson⁶⁶ says, "Any of the electrons in an octet might act in this way to fill gaps in the layers of electrons around an atom. Thus an octet might act as a nucleus from which chains and side chains of atoms ramified in every direction. As far as geometrical considerations are concerned, there is nothing to limit the number of certain atoms which could be linked together in this way."

In this structure, it will be noted that there are four molecules of hydrofluoric acid and that one molecule differs from the other three. In the organic hydrofluorides the first molecule to attach itself to the amino group is rendered relatively more positive than the other acid molecules, which is the condition under which this structure is assumed to be possible of formation. Similarly in the potassium fluoride, the fluorine atom attached to the potassium is rendered relatively positive and thereby allows the formation of a compound of the structure $\text{KF}\cdot\text{3HF}$.



In this conception of the structure of the organic compounds the reason why one of the acid molecules is not readily titrated and the other three are so easily determinable is apparent. The three hydrofluoric acid molecules attached through their hydrogen atoms are very readily hydrolyzed while the other acid group is strongly attached to the amino group. This conception of fluoride derivatives would also allow such compounds as $\text{KF}\cdot\text{HF}$, $\text{KF}\cdot\text{2HF}$ and the corresponding organic compounds, (Ref. to 6 and 8), for it would not be essential or necessary for all the electrons of the fluorine atom to be shared. This complete sharing would be the tendency in the presence of an excess of hydrofluoric acid.

Probably other conceptions of the structure of these compounds could be formulated, but of the several which we have considered, the one just given presents a satisfactory explanation for (1) formation of compounds of the type $\text{B}(\text{HF})_4$ or better $\text{B}\cdot\text{HF}\cdot\text{3HF}$ and $\text{K}\cdot\text{F}\cdot\text{3HF}$, (2) the possibility of formation of mono-, di- or tri-acid salts such as $\text{KF}\cdot\text{HF}$, $\text{KF}\cdot\text{2HF}$, etc., (3) the titration phenomena described in which the facts are presented to show that but three-fourths of the total hydrofluoric acid present in the molecule can be titrated directly by indicator method and (4) the improbability that more than four molecules of hydrofluoric acid may combine with a basic group (or more than three molecules with the type KF).

⁶⁶ Thomson: *Phil. Mag.*, 41, 544 (1921).

The singular properties of fluorine, as compared to other halogens, are too well known to require comment. However, under certain circumstances there are exhibited similar types of reactions.

That compounds containing more than one halogen acid molecule to each molecule of amine can exist and that such combination is a circumstance of environment has been shown by several investigators. Working with dry acids and dry bases Kaufler and Kunz⁵⁷ produced hygroscopic salts which evolved acid in the air, from dimethyl amine, dimethyl aniline, dimethyl-*o*-toluidine and other bases. In a second paper the same authors⁵⁸ described the preparation of other salts of the general formula B_2HX from numerous aliphatic and aromatic amines and pointed out that the ability to form such salts is decreased by the introduction of negative groups in the molecules. This is in direct accord with the structure presented in this paper.

Korcznski⁵⁹ has measured the quantity of pure dry hydrogen chloride absorbed by certain amines at temperatures varying from room temperature to 75°C. and found that salts were formed containing two and three molecules of hydrogen chloride to each one of base. In a second paper⁶⁰ he extended this work and summarizes his conclusions ascribing the constitution of the bodies to the coordination value of nitrogen.

From these facts it may be assumed that under the proper conditions the other halogen acids may form similar types of compounds as the hydrofluoric acid. Hydrochloric acid, being the halogen acid which, in electronic structure is most comparable to hydrofluoric acid, would naturally form acid salts far more readily than hydrobromic or hydriodic acids. No doubt, judging from the difficulty in preparing acid hydrochloride salts, it would be rather improbable that even relatively stable acid bromides or iodides could be prepared.

Summary

Evidence has been presented to prove that whenever an organic amine is treated with an excess of hydrofluoric acid the resulting compound has a base to acid ratio of 1:4; i.e. an empirical composition of $B.(HF)_4$.

It has been demonstrated by electrometric titration studies that of the four molecules of acid attached to the base, three are bound and react in an identical manner, while the fourth differs distinctly from these in the nature of its reactions and union to the base.

The work of previous investigators in this field has been discussed and their results, though apparently quite different, are shown to actually be in complete accord with those herein reported.

An attempt has been made to present an explanation of this phenomena and to correlate this unusual behavior with the inorganic compounds of

⁵⁷ Kaufler and Kunz: Ber., 42, 385 (1909).

⁵⁸ Kaufler and Kunz: Ber., 42, 2482 (1909).

⁵⁹ Korcznski: Ber., 41, 4379 (1908).

⁶⁰ Korcznski: Ber., 43, 1820 (1910).

hydrofluoric acid as well as with some of its general physical and chemical properties.

A structure is proposed for this type of compound which appears to satisfactorily explain the formation of compounds of the type $B.HF_3HF$, the possibilities for the formation of compounds containing less but no more hydrofluoric acid and the fact that but three-fourths of the acid present is directly titratable acidimetrically.

Acknowledgment

The authors wish to express their deep appreciation to Professor William Mansfield Clark for the many helpful suggestions regarding the electrometric studies of the compounds described and to Dr. William Blum for generously allowing us to use the electrometric apparatus and the facilities of the Electrochemical Division of the United States Bureau of Standards.

A SIMPLE METHOD FOR MEASURING ROTATORY DISPERSION

BY ISAAC BENCOWITZ

Introduction

The importance of rotatory dispersion has been well recognized both by physicist and chemist. While the general apparatus for polarimetric measurements has considerably improved and is available in every well-appointed laboratory, the measurement of rotatory dispersion has been confined to very few laboratories. This is due to the fact that this field of work is still one of the most difficult in experimental physics.

The chief difficulty lies in the lack of light sources of sufficient purity and intensity for polarimetric measurements. The increase in the intensity of a nearly monochromatic source of light is usually accompanied by a decrease in its homogeneity, while accurate polarimetry demands both intensity and homogeneity. Furthermore, in dispersion work where several hundred readings are taken in a single day, it is very essential that the source of light should be steady, free from flickering or "running." Flames, therefore, even if they were of sufficient homogeneity cannot be employed in extensive measurements. Metallic arcs suffer from the same disadvantage. Even the best rotating arcs do not provide a steady source of illumination. When either flames or arcs are used, very elaborate spectroscopic apparatus must be employed to purify the light, and it is physically impossible for one man to make measurements and keep the sources adjusted simultaneously.

The enclosed arc is the only source of light suitable for polarimetric work. Unfortunately, we are confined, at present, to the mercury arc, giving only two lines of sufficient intensity and homogeneity for dispersion measurement.

Cadmium gives a spectrum which in conjunction with the mercury arc is ideal for dispersion measurements. It has four intense lines sufficiently apart in the spectroscope scale to make elaborate monochromators unnecessary. These four lines together with the two mercury lines cover practically the entire range of the visible spectrum. Unfortunately, the difficulty of producing a cadmium lamp which burns steadily and gives out light of high intensity has been so great, that the four cadmium lines have been used only very occasionally in optical experiments.

Lowry and Adams¹ used a quartz cadmium vapor lamp for dispersion measurements. It was later improved by Sand², but it still required the continuous use of a pump and frequent refilling. Bates³ succeeded in building an enclosed cadmium quartz lamp devoid of all the inconveniences of the arcs of previous workers. He used a mixture of metallic gallium and cad-

¹ Lowry and Adams: *Trans. Faraday Soc.*, 10, 103 (1914).

² Sand: *Proc. Phys. Soc.*, 28, 94 (1915).

³ Bates: *U. S. Bureau of Standards, Sci. Paper*, 371, 16 (1920).

mium. Gallium, however, is costly and difficult to obtain. The construction of the lamp is still far from a simple process.¹

These considerations make enclosed cadmium quartz lamps unavailable for chemical laboratories, and as long as we are confined to the mercury arc as the sole source of light for dispersion measurement, this important approach to many physico-chemical problems will remain inaccessible.

It has been our aim to develop a method so simple as to make the measurement of rotatory dispersion generally available for ordinary routine measurements of the laboratory. The method described below does away with the necessity of a cadmium quartz lamp, and other expensive apparatus. Moreover, it enables us to employ practically any line in the visible spectrum and as many as are needed.

It was recognized at the outset that many applications of rotatory dispersions require the highest degree of accuracy. For most chemical investigations, on the other hand, the purity of the substances studied is such that the highest precision is unnecessary. In such cases, especially where only the visible range of the spectrum is desired, an accuracy of 0.02 of a degree is sufficient.

Continuous Spectrum as a Source

The continuous spectrum of the sun was the first source of light employed in polarimetric work.²

Lippich³ employed an artificial continuous spectrum in conjunction with a direct-vision spectroscope. He passed the light through a spectroscope the eye-piece of which was replaced by a narrow slit, which served as a source of light for the polarimeter.

The chief source of error inherent in the use of a continuous spectrum is the effect of stray light. In addition, the ordinary methods of calibrating a spectroscope are unsatisfactory. These methods, besides being cumbersome, require additional apparatus, which is rather expensive and is often not available even in the best chemical laboratories. Moreover, most spectroscopes used in conjunction with polarimeters will not "stay" calibrated. This necessitates frequent recalibration. The most fundamental objection, however, lies in the fact that the wave length of the optical center of a patch of continuous spectrum is not the wave length obtained by the calibration of the prism with a monochromatic source. Moreover, the optical center of gravity of a patch of continuous spectrum varies with the intensity of the source of power and the width of both the slit at the collimator and at the telescope ends.

On the other hand, a continuous spectrum employed as a source of light in rotatory dispersion measurements offers several important advantages. It provides a steady source of light which requires hardly any care. Its position

¹ The Cooper Hewitt Company, however, has lately succeeded in building a cadmium-gallium arc for us, the construction of which took them almost a year and was possible only because of their untiring effort and interest in the success of the undertaking.

² Brach: *Ann. Chim. Phys.*, 34, 119-121 (1852).

³ *Sitzungsber. Akad. Wiss. Wien*, 91 II, 1970 (1885).

relative to the optical axis of the apparatus is not disturbed; any desired intensity may be obtained; and any wave length of the spectrum is attainable.

It is because of these obvious advantages of a continuous spectrum on the one hand, and the enormous difficulties encountered in the use of other sources of illumination, on the other hand, that we have attempted to develop a method based on the use of a continuous spectrum.

The considerations of the following section suggest such a method.

Theoretical Considerations

The method for measuring rotatory dispersions developed in this paper is based on the following considerations:

A beam of white light passing through a narrow slit of the collimator and incident upon a prism is dispersed into a continuous spectrum. If the eyepiece at the telescope end of the spectroscop is replaced with another slit similar to that at the collimator end, we are enabled to isolate a narrow patch of light of the continuous spectrum. Let the opening of the slit be such that the patch of light transmitted consists of several wave lengths, $\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_k$.

The telescope-end slit then serves as a source of light for the polarimeter. The patch of light, having been polarized, is then rotated by an optically active medium placed in its path between the polarizer and the analyzer.

The rotation of the planes of polarization by an optically active substance is different for different wave lengths, and the section of spectrum incident upon the polarimeter will be further resolved before it reaches the analyzer. The extent of this resolution will depend upon the dispersion curve of the optically active substance, and the total magnitude of the rotation. If the width of the slit is such that the difference $\alpha_1 - \alpha_k$ is considerable, the illuminated portion of the field will not be totally extinguished, but as the analyzer is rotated a dark band will appear and disappear intermittently. The setting of the analyzer corresponding to the various dark bands will give the rotations $\alpha_1, \alpha_2, \dots, \alpha_k$ of the plane of polarization of the wave-lengths $\lambda_1, \lambda_2, \dots, \lambda_k$ respectively. If, on the other hand, the width of the slit is made narrow so that $\Delta\lambda$ is small, the intermittent dark bands will not appear when viewed at the analyzer-end. But the difference between α_1 and α_k may still be too large and the patch of light will not be completely extinguished. However, $\Delta\lambda$ can be made still smaller by closing the slit further so that the magnitude of the difference of the total rotation is reduced sufficiently to obtain perfect extinction. The width of the illuminated band due to the difference between α_1 and α_k even when perfect extinction is obtained may still be considerable and the average rotation recorded by the analyzer will lie somewhere between α_1 and α_k . This mean rotation, α_c , will depend upon the distribution of the energy intensities among $\lambda_1, \lambda_2, \dots, \lambda_k$.

It is possible, at least abstractly, to find a monochromatic source of wave length λ_m such that when polarized its plane of polarization will be rotated by the given optical substance to the same extent as that of the non-homogeneous patch of light. That is, if α_c is the rotation of a non-homogene-

ous source and α_m the rotation of the corresponding monochromatic source, then $\lambda_o = \lambda_m$. We define λ_o as the wave length of the "polarimetric" optical mean of the patch of light of continuous spectrum consisting of $\lambda_1, \lambda_2, \dots, \lambda_k$ such that $\lambda_o = \lambda_m$. It is a theoretical wave length of a monochromatic source that would give a rotation equivalent to that of the entire band $\lambda_1, \lambda_2, \dots, \lambda_k$. It is not necessarily identical with the optical center of gravity determined spectroscopically, i.e. one dependent upon the distribution of energy and wave length. The optical mean as defined here depends upon the inherent characteristics of optical activity.

The value of the "polarimetric" optical mean, λ_o , as defined above can be obtained by means of any optically active substance whose dispersion curve is known, simply by measuring the rotation of the plane of polarization of the patch of light and determining from the dispersion curve the corresponding λ_m . Or given a definite λ_m the corresponding α_m is obtained from the dispersion curve or available tables for the standard substance. The prism of the spectroscope is then moved until the patch of light illuminating the polarimeter is such that the standard substance rotates its plane of polarization to the extent of $\alpha_o = \alpha_m$. The optical mean of that patch of light is then $\lambda_o = \lambda_m$. We thus establish a correspondence between definite patches of light in terms of monochromatic sources.

Any substance, the rotatory dispersion curve of which is known, can be employed as a standard. However, the question arises, will the polarimetric optical mean determined by any one substance be identical with that determined by another, the dispersion curve of which is different?

A cursory analysis of the characteristics of polarimetry as well as of the results given in Table I seem to indicate an affirmative reply. The width of the illuminated band to be extinguished by the analyzer will depend upon the magnitude of the difference between the terminal wave lengths of the patch of light incident upon the polarimeter and the difference between the corresponding rotations of α_1 and α_k . The differences between λ_1 and λ_k is kept constant by maintaining the same width of the slit, and is, therefore, independent of the optical substances employed. The difference of the total rotations α_1 and α_k , on the other hand, will depend upon the dispersion curve of the substance and the magnitude of the rotations. However, the rotation α_o recorded by the analyzer is the mean of $\alpha_1, \alpha_2, \dots, \alpha_k$ and for patches of light sufficiently narrow to give complete extinction, the mean will be independent of the width of the band $\alpha_1 - \alpha_k$. The value of λ_o determined by one substance will, therefore, be identical with that determined by another substance and independent of their respective dispersion curves. This conclusion may not be rigorous but that it is valid within the precision justified by the purity of most optically active substances is established by the data given below.

Quartz is an ideal substance to be employed as a standard. Its dispersion curve¹ and its temperature coefficient² have been accurately determined. The

¹ T. M. Lowry: Phil. Trans., 212A, 261-297; Lowry and Coode-Adams: 226 A, 391-466 (1927).

² U. S. Bureau of Standards Circular, No. 44, 18 (1918).

fact that quartz test plates are employed in saccharimetry makes it possible to procure them in various thicknesses and convenient form. The plates are rigidly enclosed in metallic frames adjusted to fit the polarimeter. The United States Bureau of Standards is equipped to calibrate the thickness of the plates as well as their optical rotation for several wave lengths.

Experimental Procedure and Results

A Schmidt and Haensch polarimeter provided with a direct-vision spectro-scope was employed in all measurements. A quartz mercury arc served as a source of monochromatic light and a small electric bulb with a horizontal tungsten filament was used as the source of non-homogeneous light. This lamp was mounted on brackets attached to the spectroscope so that when the direct vision prism was rotated the lamp remained focused.

A quartz test plate supplied by Bausch and Lomb and calibrated in the Bureau of Standards was employed as a standard. The solutions were kept in jacketed tubes and the temperature was maintained at $25^{\circ}\text{C} \pm 0.01$ by means of a rapid stream of water from a thermostatic bath.

The polarimeter was first tested by means of the quartz plate for the mercury green line, 5461 Å, and the mercury violet, 4358. The average of twenty readings checked with the values of the Bureau of Standards to within ± 0.01 , which is well within the error of the apparatus.

The values in Table I were obtained in the following manner. A solution of an optically active substance was placed in the polarimeter, and the rotation of the plane of polarization of the Hg-green, 5461, with the mercury arc as a source of light was determined. These values are recorded under α_m in column 2. The mercury arc was then replaced by the incandescent lamp and a narrow patch of its continuous spectrum was focused upon the analyzer. The quartz plate was then placed in the polarimeter, and the prism of the spectroscope adjusted so that the optical center λ_0 of the patch of light passing through the slit of the telescope-end was equivalent to 5461. That is, the prism was moved until the plane of polarization of the patch of light was rotated by means of the quartz plate to the same extent α_q as that given by the Bureau of Standards for monochromatic green of 5461 Å. The quartz plate was then replaced by the solution and its rotation determined. These values are given in Table I, column 3. In determining the value of α_q , the zero point of the apparatus was added to the required reading of the quartz plate and the temperature correction was applied. In the case of the solution, the zero point of the tube was determined before filling and subtracted from the reading.

The above procedure was repeated with mercury violet, 4358 Å, the results of which are given in columns 5 and 6 and for mercury yellow in columns 8 and 9. In the latter case, the optical centers of both the mercury arc and the continuous spectrum were found by means of the quartz plate.

Solutions of various concentrations giving a total rotation from 50.00° to 3.00° were employed.

TABLE I
 Comparison Values of the Rotation α_m of a Monochromatic Source of Light λ_m and α_c , the Mean Rotation of a Patch of Non-Homogeneous Light the Optical Center of Mass of which is λ_c equivalent to λ_m

| α_m | Hg-green; 5461 Å | | Hg-violet; 4359 Å | | Hg-yellow; 5700 | |
|------------|------------------|------------|-----------------------------------------------|------------|-----------------|------------|
| | α_c | Difference | α_c | Difference | α_c | Difference |
| 1.88 | 1.88 | 0.00 | | | | |
| 10.25 | 10.23 | -0.02 | | | | |
| 11.07 | 11.09 | +0.02 | | | | |
| 15.30 | 15.30 | 0.00 | 15.54 | +0.03 | 9.34 | -0.02 |
| 17.40 | 17.43 | +0.03 | 25.55 | +0.03 | 10.00 | +0.01 |
| 19.22 | 19.22 | 0.00 | 29.03 | -0.02 | 13.37 | +0.02 |
| 22.00 | 21.98 | -0.02 | 32.00 | -0.03 | 15.31 | -0.01 |
| 24.89 | 24.90 | +0.01 | 36.26 | +0.02 | 16.85 | -0.05 |
| 27.60 | 27.61 | +0.01 | 40.94 | -0.04 | 19.31 | -0.01 |
| 39.01 | 38.98 | -0.03 | 46.06 | -0.02 | 21.90 | +0.03 |
| 47.16 | 47.16 | 0.00 | 79.18 | +0.04 | 24.16 | 0.00 |
| | | | 79.22 | +0.04 | 42.74 | +0.01 |
| | | | β-Mannose Pentacetate | | | |
| -0.59 | -0.58 | -0.01 | | | | |
| -2.37 | -2.36 | -0.01 | 3.86 | -0.02 | 2.11 | -0.01 |
| -3.52 | -3.52 | 0.00 | 6.94 | -0.02 | 2.98 | -0.01 |
| -8.97 | -8.98 | -0.01 | 14.80 | -0.01 | 7.92 | +0.01 |
| -11.22 | -11.22 | 0.01 | 18.28 | -0.01 | 9.93 | +0.01 |
| -12.35 | -12.36 | +0.01 | 20.06 | -0.02 | 10.95 | +0.01 |
| -16.38 | -16.36 | -0.02 | 26.63 | -0.01 | 14.49 | +0.01 |
| -16.97 | -16.98 | +0.01 | | | | |
| | | | Tartaric Acid in Water | | | |
| 2.11 | 2.10 | -0.01 | | | | |
| 4.17 | 4.15 | -0.02 | | | | |
| 5.61 | 5.62 | +0.01 | | | | |
| 7.10 | 7.10 | 0.00 | | | | |
| 9.40 | 9.42 | +0.02 | | | | |
| | | | 1.75 | 1.75 | 1.75 | 0.00 |
| | | | 3.80 | 3.78 | 3.78 | -0.02 |
| | | | 5.17 | 5.15 | 5.15 | -0.02 |
| | | | 6.65 | 6.64 | 6.64 | -0.01 |
| | | | 9.10 | 9.11 | 9.11 | +0.01 |

The differences between the rotation of a non-homogeneous patch of light α_o , and that of a monochromatic source of light α_m , are given in columns 4, 7 and 10. The close agreement between the two is remarkable in view of the fact that the dispersion curves of the three substances employed are different.

The dispersion curves of the pentacetates of α -Mannose and β -Mannose are accurately expressed¹ by one term of Drude's equation $\alpha = \Sigma \frac{K}{\lambda^2 - \lambda_o^2}$. The

dispersion curve of tartaric acid, on the other hand, is reproduced by² $\alpha = \frac{K_1}{\lambda^2 - \lambda_1^2} - \frac{K_2}{\lambda^2 - \lambda_2^2}$ while that of quartz is given by $\alpha = \frac{K_1}{\lambda^2 - \lambda_1^2} + \frac{K_2}{\lambda^2 - \lambda_2^2} + \frac{K_3}{\lambda^2}$.

In obtaining the data given in Table I, only the ordinary precautions of routine measurements were observed. No attempts were made at more painstaking accuracy; otherwise the agreement might have been much closer.

Experimental Procedure in Measurements of Rotatory Dispersion

The details of the following method are a description of the procedure used in obtaining the data published elsewhere. The following wave lengths were chosen: Li, 6708 red; Cd, 6438 red; Zn, 6364 red; Cu, 5790 yellow; Hg, 5700 yellow; Hg, 5461 green; Tl, 5351 green; Cd, 5086 green; Cd, 4800 blue; Hg, 4359 violet. The rotations, α_{Li} , α_{Cd} , . . . $\alpha_{Hg-violet}$ of the plane of polarization of the corresponding wave lengths by our quartz plate were calculated from the known thickness of the plate and the data given by Lowry.

With the incandescent lamp as a source, the prism of the spectroscope was rotated until the patch of light passing through the slit of the telescope-end was red and the zero point of the empty tube for the red region of the spectrum was determined. Similarly, the zero point of the empty tube was determined for the green, blue and violet regions. It was found by preliminary measurements that the zero point of the tube did not vary much for wave lengths within each region.

The zero point of the tube having been determined, the tube was filled with the solution and allowed to come to the temperature equilibrium. Meanwhile, the quartz plate was placed in the polarimeter and the prism of the spectroscope moved until the patch of light passing through the quartz plate was such that its rotation by the plate was equal to that of α_{Li} , plus the zero point of the apparatus for red. The tube with the solution was then put in place of the quartz plate and the rotation of the same patch of light by the solution was measured. The quartz plate was again substituted and the setting of the spectroscope checked. Whenever the two readings did not agree, the spectroscope was reset and the readings with the solution repeated. As a rule, the spectroscope seldom needed resetting. This procedure was repeated for the ten wave lengths. At least fifteen readings were taken for each

¹ P. A. Levene and I. Bencowitz: J. Biol. Chem., 72, 627; 74, 153 (1927).

² T. M. Lowry and P. C. Austin: Phil. Trans., 212 A, 249-308 (1922).

setting. To check the readings as well as to determine whether any change in the concentration took place during the measurements, the entire procedure was repeated from Li red to Hg violet. Rarely did the average of the two sets of readings differ by more than ± 0.02 , notwithstanding the fact that often as long as six hours elapsed between the two sets of readings.

Conclusion

The procedure described in this paper provides a means for measuring rotatory dispersions which requires no cadmium quartz lamp or other expensive apparatus. The technique is simple and with a little experience it is possible to make a complete determination for ten wave lengths in five hours. It is accurate to within 0.02° and the purity of most optically active substances does not justify higher precision. This method likewise enables us to employ any wave length the rotation of which in quartz is known.

I take this opportunity of thanking Dr. P. A. Levene for suggesting the problem and for much valuable advice.

Summary

A simple substitution method of measuring rotatory dispersion is described.

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THE INFLUENCE OF MOVEMENT OF ELECTROLYTE UPON THE STEADINESS OF THE POTENTIAL OF THE OXYGEN ELECTRODE

BY H. V. TARTAR AND VICTOR E. WELLMAN

All efforts to determine experimentally the potential of a reversible oxygen electrode and of the hydrogen-oxygen cell, have failed because of the apparent irreversibility of the reaction occurring at the electrode surface or of the formation of oxides of the metal electrode used. Different workers¹ have obtained widely different values for the potential using a given electrolyte. Furthermore, the potential is not steady but has a tendency to "drift" from 5 to 10 millivolts per hour in acid solution to 30 to 60 millivolts² in alkaline solution. Reference oxygen electrodes³ of unsteady potential have apparently been utilized satisfactorily in a limited way for certain electrometric measurements. This brief paper is presented in the hope that the findings may serve the purpose of making the oxygen electrode more useful as a reference electrode and also of suggesting new lines of investigation for ascertaining the nature of this perplexing electrode.

While studying the depolarizing effect of an intermittent alternating current upon the potential of an oxygen electrode, it was found that agitation of the electrolyte influenced the potential to a marked and fairly reproducible degree; in fact, slow bubbling of oxygen through the electrolyte around the electrode had a greater influence upon the potential than an intermittent, 60-cycle alternating current at 10 volts across the cell. The results given below have been secured from a limited study of the influence of the *movement of the electrolyte* upon the potential of oxygen electrodes in acid, neutral and alkaline solutions.

The apparatus shown in Fig. 1 was used for obtaining the most consistent results. The electrolyte was placed in reservoir R, where it was saturated with oxygen by bubbling the gas into the solution at atmospheric pressure. Commercial electrolytic oxygen was passed through acidified potassium permanganate, then through dilute sodium hydroxide and finally through distilled water before it was passed into the electrolyte in the reservoir. The flow of the liquid from the reservoir through the apparatus was regulated by means of a screw clamp (S).

The electrolyte was brought to constant temperature, $25^{\circ}\text{C} \pm 0.05^{\circ}$, in a large glass coil submerged in a water thermostat before it entered the electrode vessel (V) through the side tube (A). The liquid was maintained at constant level (L) by the side arm opening (O). The electrode vessel was also kept in the thermostat and held at constant temperature.

¹ Grube: *Z. Elektrochemie*, 24, 237-48 (1918); Foerster: *Z. physik. Chem.*, 69, 236-71 (1910); Lorenz: *Z. Elektrochemie*, 14, 781-3 (1908).

² Furman: *J. Am. Chem. Soc.*, 44, 2685 (1922).

³ Furman: *loc. cit.*

The stopper of the electrode vessel (V) held three electrodes near the opening at the side tube (A). The electrodes were made by sealing platinum wire into small glass tubes, connection with the potentiometer leads being made through mercury. In order that the electrodes might be under conditions as nearly identical as possible, they were placed close together, nearly parallel and about 3 mm. below the level of the liquid (L). The platinized electrodes were prepared by electrolyzing a one per cent solution of chlor-

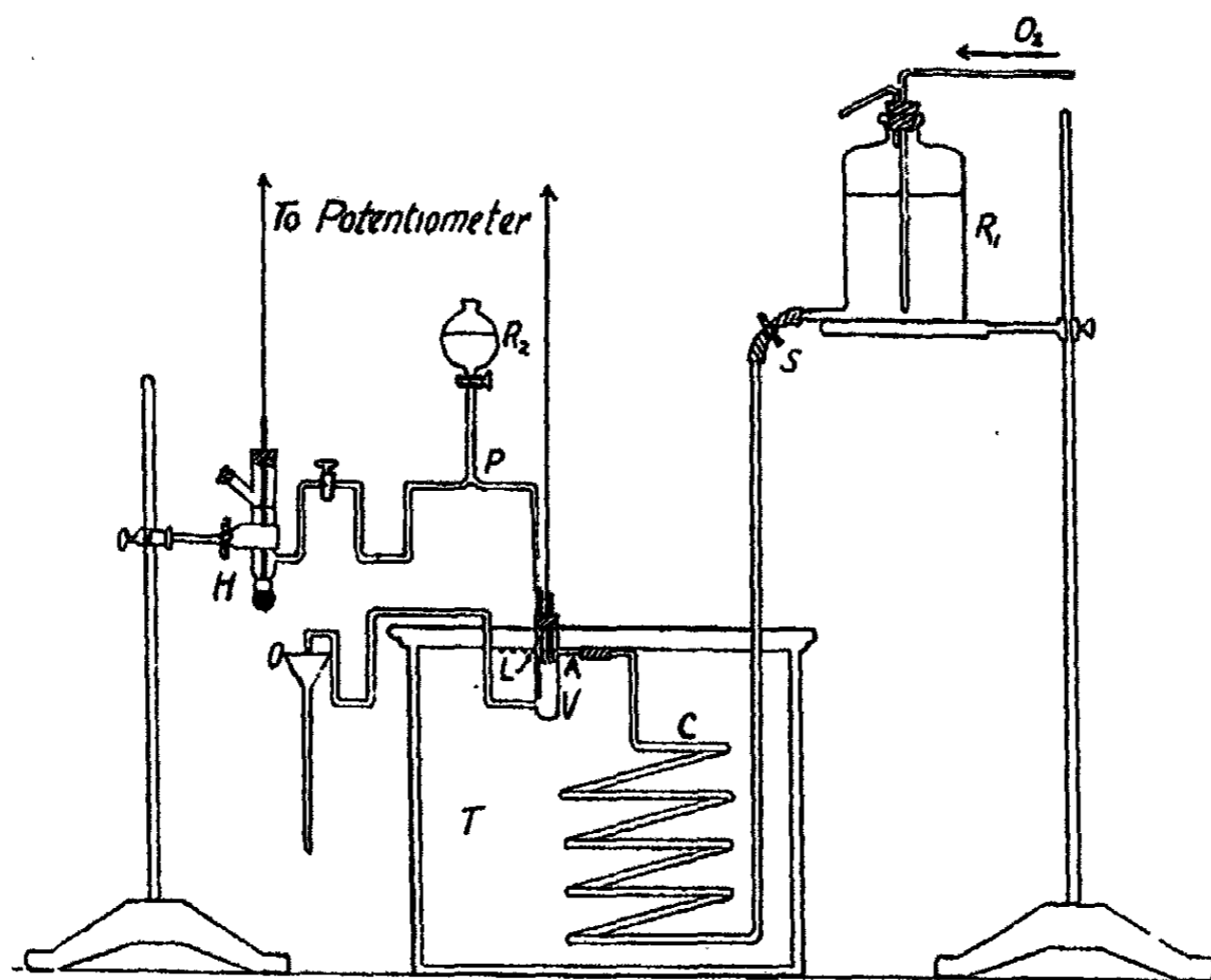


FIG. 1

platinic acid, the current being reversed approximately every ten seconds. Before use, the electrodes were soaked in sulfuric acid-dichromate cleaning solution after which they were soaked in water for several hours.

Any bubbles entering accidentally into the connecting tube to the normal calomel electrode could be made to rise to the point (P) thus insuring unimpaird electrolytic contact with the liquid in the electrode vessel. The reservoir, (R₂), contained normal potassium chloride solution which was used when necessary to flush the tip of the connecting tube from the calomel half cell to the bottom of the electrode vessel, (V).

The potentials were read with a Type K, Leeds and Northrup potentiometer set with a Weston standard cell certified by the Bureau of Standards. The potentials reported in the Tables have been calculated to the normal hydrogen reference electrode, taking the potential of the normal calomel electrode to be -0.283 volts.¹

¹ Lewis and Randall: "Thermodynamics," 407 (1923).

It was found convenient to regulate the rate of flow by observing the rate at which the liquid dropped from the tube at the point, (O). In the tables the flow of electrolyte is given as the number of drops per second. Under ordinary conditions eleven drops delivered about one cubic centimeter of electrolyte.

In order to make clear to the reader why bright platinum electrodes were used, it may be well to give first the results of some preliminary experiments carried out with an apparatus more simple in design than that described above. These experiments were made using one electrode at a time without thermostatic control and without careful regulation of the rate of flow of the electrolyte; consequently, the conditions under which different electrodes were tried were not closely identical. The results obtained, however, showed that there was a greater tendency for "drift" of potential with platinized electrodes than with bright platinum electrodes: the heavier the platinization the greater the "drift." In one instance the potential changed 0.18 volts in six and one-half hours with a heavily platinized electrode in alkaline solution. Using the same electrolyte, heavily platinized electrodes gave potentials which were extremely unsteady and variable. Bright platinum surfaces, while not exactly uniform, afford conditions much better adapted for the reproducibility of potentials; for this reason bright platinum electrodes were used in the major part of this investigation.

Following the preliminary work which showed the marked influence of the platinum surface and the movement of the electrolyte; a series of experiments were made using bright and very lightly platinized electrodes with acid, neutral, and alkaline solutions. It is not essential, to present all of the

TABLE I
Oxygen Potentials with Platinum Electrodes in Normal Sulfuric Acid

| Time (Minutes) | Potential Bright platinum Electrode No. 1 | Potential Bright platinum Electrode No. 2 | Potential Platinized platinum Electrode No. 3 | Rate of flow of electrolyte |
|-------------------|----------------------------------------------------|----------------------------------------------------|-----------------------------------------------------------|-----------------------------------|
| 0* | -0.805 | -0.795 | -0.951 | 19 drops in |
| 10* | -0.805 H | -0.795 H | -0.951 H | 30 seconds |
| 15* | -0.798 H | -0.788 L | -0.933 L | Approximately |
| 40 | -0.793 H | -0.788 L | -0.938 L | 4 cc per |
| 45 | -0.791 | -0.791 H | -0.943 H | minute. |
| 50 | -0.791 H | -0.789 | -0.938 H | |
| 55 | -0.788 | -0.788 | -0.933 H | Rate main- |
| 60 | -0.788 | -0.788 L | -0.928 H | tained |
| 65 | -0.788 L | -0.788 | -0.918 H | throughout. |
| 85 | -0.789 L | -0.788 | -0.903 H | |
| 95 | -0.790 L | -0.788 | -0.883 H | |
| 120 | -0.791 | -0.788 | -0.881 L | |
| 135 | -0.791 L | -0.788 L | -0.878 | |

* High initial values probably due to electrolyte not yet being saturated with oxygen.

data obtained. For the purpose of this paper it will suffice to present the data from typical experiments using simultaneously three electrodes with the conditions as nearly identical for the electrodes as could be obtained. The results of two experiments are given: one using normal sulfuric acid as the electrolyte, reported in Table I; and one with 1.149 normal sodium hydroxide, Table II. The electrodes referred to in the data as "lightly platinized" were prepared from thoroughly cleaned bright platinum wire which was platinized for less than a minute with a current density just sufficient to give slight bubbling of gas at the cathode; the deposit of platinum black was just sufficient to remove the glint from the bright surface.

TABLE II
Oxygen Potentials with Platinum Electrodes in 1.147 Normal Sodium Hydroxide

| Time (Minutes) | Potential Bright platinum Electrode No. 1 | Potential Bright platinum Electrode No. 2 | Potential Platinized platinum Electrode No. 3 | Rate of flow of electrolyte |
|----------------|-------------------------------------------|-------------------------------------------|-----------------------------------------------|-----------------------------------------------------------------------------|
| 0 | -0.147 | -0.148 | -0.187 | 1 drop per second |
| 15 | -0.147 | -0.147 L | -0.187 L | ↓ (Flow slightly increased. 4 drops per sec. Flowing freely Flow stopped |
| 25 | -0.147 | -0.150 | -0.187 L | |
| 40 | -0.147 | -0.153 L | -0.190 L | |
| 55 | -0.147 | -0.156 | -0.192 | |
| 70 | -0.148 | -0.156 | -0.192 | |
| 85 | -0.148 L | -0.156 | -0.192 H | |
| 100 | -0.149 | -0.156 H | -0.190 | |
| 115 | -0.149 | -0.155 H | -0.190 H | |
| 130 | -0.149 H | -0.148 | -0.189 H | |
| 145 | -0.148 | -0.148 | -0.190 H | |
| 160 | -0.148 | -0.148 | -0.189 L | |
| 175 | -0.148 H | -0.148 L | -0.190 | |
| 190 | -0.147 L | -0.150 | -0.190 | |
| 205 | -0.148 | -0.150 | -0.190 H | |
| 220 | -0.148 | -0.149 | -0.189 | |
| 235 | -0.148 L | -0.149 | -0.189 | |
| 250 | -0.143 | -0.146 | -0.179 | |
| | -0.138 | -0.140 | -0.172 | |
| | -0.145 | -0.143 | -0.178 | |
| | -0.143 | -0.139 | -0.179 | |
| 265 | -0.139 | -0.134 | -0.177 | |
| | -0.138 | -0.118 | -0.181 | |
| | -0.134 | -0.127 | -0.189 | |
| | -0.129 | -0.125 | -0.193 | |
| | -0.133 | -0.130 | -0.190 | |
| | -0.134 | -0.126 | -0.178 | |
| 290 | -0.130 | -0.117 | -0.173 | 7 ml. per minute. |
| 295 | -0.133 | -0.128 | -0.177 | { 25 ml. per min. |

Some difficulty was experienced in reading the potentials in neutral and acid solutions. It was found that in these solutions the potentiometer could be set anywhere within a range of 40 to 60 millivolts and the galvanometer finally show no deflection if the connecting key were tapped frequently enough. This apparent "balance," obtained both above and below the actual potential, was possibly due to the influence of sending a small current through the cell when the potentiometer was "off balance." In alkaline solution this apparent shifting of potential was not encountered. With acid and neutral solutions, the actual potential could be ascertained by tapping the connecting key once only at intervals not less than five minutes. If the potentiometer reading was too high as shown by the galvanometer deflection it was set lower for the next reading; and if too low, set somewhat higher. The actual potential could be closely followed after a little practice. Some of the potentials given in Tables I and II are not exact; when slightly high (as shown by tapping connecting key once) they are followed by the letter H and if low by the letter L.

Some experiments were performed using one electrode at a time with tenth-molar potassium sulfate solution as the flowing electrolyte. The potentials were also steady with bright and lightly platinized electrodes provided the rate of flow of the solution was maintained constant. The potentials of the bright platinum electrodes were reproducible within 20 to 30 millivolts. With the platinized electrode the potential was approximately 0.35 volt higher than with bright platinum.

Discussion of Results

The data presented above show that the potential of the oxygen electrode is greatly stabilized by the steady movement of the electrolyte past the electrode. The fluctuations occurred in both directions and there was no evidence of the "drift" of potential in a given direction mentioned by previous investigators.¹ The steadiness of potential reported herein differs greatly from the results reported in the literature. Schoch², in his review of the literature on the oxygen electrode, states that potentials varying from 1.5 to 0.008 volts have been reported for the oxygen-hydrogen cell.

The effect of change of rate of flow of the electrolyte on the potential was much more pronounced in alkaline than in acid or neutral solution. This finding is, no doubt, related to the greater rate of "drift" of potential in alkaline solution reported by previous workers. The surface conditions of the electrode apparently exert a considerable influence on the potential; heavily platinized electrodes are affected to a greater extent than other types by the rate of flow of the solution.

The data presented above indicate the possibility of reproducibility of oxygen electrode potentials when bright platinum is used for the electrode metal. The results indicate that, regardless of the acidity or alkalinity of

¹ Furman: *loc. cit.*

² Schoch: *J. Phys. Chem.*, 14, 665 (1910).

the solution, the potential of a bright platinum wire electrode in a given solution can be held with a variation not exceeding three millivolts provided the flow of the liquid is carefully controlled. The lack of reproducibility experienced by other investigators has evidently been due in large measure to dissimilarity inherent in platinized surfaces; first, the amount of platinization is not exactly reproducible and second, the platinum deposited is not uniform in texture. Britton¹ using platinized platinum, found that he could not prepare two oxygen electrodes which gave the same potential in a given solution.

The fact that apparently correct potential values over a range of approximately 60 millivolts may be secured in neutral and acid solutions by proper "setting" of the potentiometer and manipulation of the tapping key in the circuit, leads one to suspect that many of the potentials reported in the literature may be of but little significance. This "manipulation" of the potential can be accomplished over a wider range with platinized electrodes than with the bright metal. Whether this phenomenon may be used to furnish an adequate explanation of the various "resting points"² or "steps" in the oxygen potential, is not known.

For a considerable time the anomalous behavior of the oxygen electrode has been usually ascribed to the formation of oxides of platinum. Schoch reports that experimenters have, "with special manipulation," obtained potentials which have been claimed to correspond to the potentials of several platinum oxides, some of which have been prepared. The various "resting points" or "steps" observed in the "drift" of the potential of the oxygen electrode have been attributed to reductions of a series of insoluble platinum oxides ranging in composition from PtO_4 to PtO , some of them supposedly in hydrated form. Gradual change of potential has been said to be due to the formation of solid solutions of one oxide in another.

The results presented in this paper do not lend themselves to simple explanation by assuming oxide formation. It does not seem probable that a slight decrease in the rate of flow of the liquid past the electrode should permit the oxidation of the platinum with the possible formation of a higher oxide. Nevertheless, a shifting of the potential away from zero usually accompanied a decrease in the rate of flow of the solution.

A more plausible explanation would be to assume the presence of a soluble substance such as hydrogen peroxide at the surface of the electrode. If this substance takes part in the electrochemical reaction, then the concentration in the electrolyte around the electrode would be affected by the rate of flow of the liquid and this change of concentration would influence the potential. Over twenty years ago, Lewis³ suggested that the values obtained for the oxygen-hydrogen cell might be due to the fact that the product of the primary reaction, is hydrogen peroxide instead of water. Tilley and Ralston⁴ state

¹ Britton: *J. Chem. Soc.*, 127, 1896-1917 (1925).

² Schoch: *loc. cit.*

³ Lewis: *J. Am. Chem. Soc.*, 28, 164 (1906).

⁴ Tilley and Ralston: *Trans. Am. Electrochem. Soc.*, 44, 31 (1923).

that "one trouble with the oxygen electrode is the uncertainty as to whether it is a true oxygen electrode (which would make it a function of the hydroxyl ion concentration) or a hydrogen peroxide electrode whose potential is determined by the combination of hydroxyl ions to form hydrogen peroxide. It is probably a combination of the two because its potential is greatly affected by the concentration of both oxidizing agents and hydroxyl ion."

The effect of hydrogen peroxide in both acid and alkaline solution was examined in a qualitative way in this work. To 300 cc of normal sulfuric acid in the reservoir (R_1), was added 1 cc of 30 per cent hydrogen peroxide solution. The potential of bright platinum electrode No. 1 was shifted toward zero 15 millivolts; that of No. 2, 5 millivolts and that of platinized platinum electrode No. 3 was shifted away from zero 7 millivolts, in a period of forty minutes. In the 1.147 normal sodium hydroxide solution, the effect was much more pronounced: the potential of electrode No. 1 was shifted toward zero 58 millivolts, No. 2, 41 millivolts and No. 3, 44 millivolts in the same length of time. It is not easily understood however, why an increase in the rate of flow of the electrolyte past the electrode should shift the potential in the same direction as is caused by adding hydrogen peroxide to the electrolyte in the reservoir (R_1).

The results presented in this paper have been obtained from but a limited study. Further work will be undertaken when opportunity provides.

Summary

(1) The effect of the rate of flow of electrolyte on the potential of the oxygen electrode has been studied and it has been shown that the potential is quite steady for a given electrode in a given electrolyte if the rate of flow remains unchanged.

(2) Under the same conditions of flow bright platinum electrodes seem to give fairly reproducible potential values; i.e. within a few millivolts.

(3) The behavior of the oxygen electrode may be more easily interpreted by the assumption of the formation of a soluble substance, possibly hydrogen peroxide, than by the so called "insoluble platinum oxide theory."

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ADHESIVES AND ADHESION: PURE CHEMICAL SUBSTANCES
AS ADHESIVES*

BY JAMES W. MCBAIN AND W. BELL LEE**

A previous paper¹ broke entirely new ground by showing that pure chemical compounds may fully rival well-known adhesives when used for joining polished metal surfaces. The breaking strength between optically polished metal surfaces may approach 1 ton per sq. in. The present communication extends these observations to other pure compounds of varied type and includes measurements on five exceptionally highly purified carbinols which had been used in the well-known work of Sir Wm. Hardy and Miss Double-day on lubrication. Definite regularities emerge showing relation between chemical constitution and adhesive power. A few preliminary measurements on joints made with wood are adduced as opening up a new possibility for the scientific investigation of glued wooden joints. One great advantage which it is found that chemical compounds present is that the strength of joints made with them is much less dependent upon time and previous heavy loading than those of many recognized adhesives.

**Homologous Series of Optically Active Carbinols between Polished
Metal Surfaces**

Dr. R. H. Pickard prepared a series of secondary carbinols of an exceptionally high degree of purity. Fifteen of these have been studied as lubricants.² Through the kindness of Dr. Pickard we have been able to use the five solid specimens.

Two sets of adhesion experiments were made (a) using ordinary carefully prepared plane steel or nickel surfaces, (b) new optically polished plane nickel and steel surfaces prepared at the National Physical Laboratory, Teddington, England. References may be made to previous papers for the kind of test pieces and method of testing joints. The loading up to fracture was completed in between one to three minutes. The effect of prolonged stress on these joints has not been investigated. All the tests made are included in the tables given in this paper. The results are not too concordant but this is inevitable where films of adhesives are exceedingly thin, because as we have shown with all sorts of joints and adhesives the joint strength increases very rapidly when the films are being made as thin as possible. This is strikingly borne out by comparison of the results in the first part of Table I with those obtained in the second part between optically trued surfaces. Where the film of adhesive between surfaces was noticeably incomplete the result is put in brackets. As is usual with all adhesives, nickel and steel

* Contribution from the chemical laboratories of Stanford University.

** Investigation undertaken for the Adhesives Research Committee of the Department of Scientific and Industrial Research, Great Britain, and published by permission of this Department.

give nearly the same strength of joint. In Table I results obtained with steel joints are put in italics. The results are calculated to the nearest 5 lbs./sq. in. The joints appeared to fail owing to rupture of the film of carbinol itself, not through failure of adhesion of carbinol to metal; the same is true of nearly all the joints mentioned in this paper.

TABLE I

Tension tests (lbs./sq. in.) of joints made between highly polished metal surfaces with specially pure optically active 1-ethyl-R-carbinols.

| R | Total C atoms | M.P. | Joint strength | | | | | Mean |
|--------------------------------------------|------------------|------|----------------|------------|------------|------------|------------|------|
| (a) Good plane surfaces of nickel or steel | | | | | | | | |
| n-decyl | 13 | 32° | 130 | <i>110</i> | <i>100</i> | 95 | 80 | 105 |
| n-undecyl | 14 | 38° | <i>215</i> | <i>215</i> | 150 | 100 | 100 | 155 |
| n-dodecyl | 15 | 45° | 275 | <i>260</i> | 255 | 250 | 235 | 255 |
| n-tridecyl | 16 | 50° | 260 | 260 | 240 | <i>210</i> | 145 | 225 |
| n-pentadecyl | 18 | 56° | 260 | <i>205</i> | 175 | 150 | <i>140</i> | 180 |
| (b) Optically plane surfaces of nickel | | | | | | | | |
| n-decyl | 13 | 32° | 570 | 450 | (245) | | | 510 |
| n-dodecyl | 15 | 45° | 775 | 775 | 650 | 650 | 610 | 670 |
| n-pentadecyl | 18 | 56° | 610 | 490 | 410 | 365 | (285) | 469 |

The results in Table I are compared in Table II with the data for static friction when the carbinols were used as lubricants for steel in the work of Hardy and Miss Doubleday. Our previous work led to the formulation of the rule that lubrication is in inverse proportion to strength of joint, that is, static friction and adhesiveness are parallel. This rule receives further confirmation in Table II. The density of the carbinol in the liquid form at 80° is included in Table II.

TABLE II

Comparison of properties in the homologous series of carbinols

| Total C atoms | M.P. | D_{40}^{80} | Static friction | | Joint strength | |
|------------------|------|---------------|----------------------|--------|----------------|-----------------|
| | | | Flooded primary film | | Plane | Optically plane |
| 13 | 32° | 0.7865 | 0.1072 | 0.1054 | 105 | 510 |
| 14 | 38° | 0.7885 | 0.0701 | 0.0684 | 155 | — |
| 15 | 45° | 0.7921 | 0.2024 | 0.2001 | 255 | 690 |
| 16 | 50° | 0.7907 | Not measured | | 225 | — |
| 18 | 56° | 0.7858 | Vanished | | 180 | 469 |

The data here assembled are of great interest in showing that density, static friction and joint strength in all cases are at a maximum in the middle of the series; that is, in the carbinol containing 15 carbon atoms. This compound was an exception to the rule that the static friction on steel or glass follows the empirical linear relation $a-bM$ where a and b are constants and M is the molecular weight. Miss Doubleday ascribed it to insufficient

purification but one of us (W.B.L.) has shown³ that there are many similar recurrent or periodic anomalies involving a large number of properties of long chain compounds such as the n-fatty acids, at multiples of 5 or 6 carbon atoms.

All the ethyl-R-carbinols are good lubricants and exhibit much poorer adhesive power than most of the pure substances so far tested, such as dextrose, trinitrotoluene, triphenyl carbinol and those mentioned in the present paper.* A good lubricant should attach itself firmly to the solid surface but should have only a feeble hold upon successive layers of molecules. It should resemble graphite rather than diamond.

An adhesive, on the other hand, whilst holding firmly to the solid surface, must likewise hold firmly to further layers of molecules thus producing static friction. It seems most probable that in such cases the first layer of oriented molecules is the starting point for chains of oriented molecules extending from it deep into the bulk of the liquid or solid adhesive.⁴ The effect of this will not only be high static friction but also the simulation of a great range of molecular attraction. This will also be closely related to the magnitude of the pull normal to the surface required to break a joint. This intimate relation between shear and tension has been observed by us in previous communications where it is often found that the two breaking strengths are equal. Corroboration of this point of view is found in the invariable rule that the thinner the film the stronger the joint, the effect being much greater when the films are as thin as possible.

One expects a parallelism between breaking strength and the cohesion of the adhesive itself, as one factor, power of forming chains of molecules being a second factor. As the homologous series is ascended the melting point which probably goes parallel with cohesion is altering in one direction, and the static friction in the other (except for the C_{15} member, where the static friction is much larger.) Hence in certain homologous series it might well happen that for a limited range the best lubricants might also be the best adhesives. In the present instance the C_{15} member stands out as the best adhesive, on account of its high static friction.

Other Pure Substances between Metal Surfaces

Similar tests of breaking strength in tension have been carried out with carefully prepared ordinary polished test pieces of metal, the adhesive being melted on to the metal. Pure stearic acid (m.p. 69°), cetyl alcohol (m.p. 49°), palmitic acid, cerotic acid and elaidic acid exemplify good lubricants whose joints are weak both in tension and in shear. Both stearic acid and cetyl alcohol give joints which are twice as strong when the film of adhesive is made specially thin by the use of optically plane test pieces in accordance

* An illustration of the antithesis between lubricants and adhesives is given by a proprietary anti-slip preparation used to prevent slipping of motor cycle belts. Aluminium usually gives far weaker joints than nickel or steel with a given adhesive, but with this preparation the joint strength in tension with ordinary aluminium test pieces was 435, 400, and 360 lbs./sq. in.; that is, several times greater than the carbinols, fatty acids or alcohols with such test pieces.

with our invariable experience. For example, the values for stearic acid with nickel were 400 and 320 lbs./sq. in. and for cetyl alcohol with steel test pieces 205 lbs./sq. in. These substances failed in the adhesive film itself, not between metal and adhesive. Inactive dihydroxystearic acid, prepared by oxidation of oleic acid has double the joint strength of the stearic acid itself and its melting point is higher. Trihydroxy-palmitic acid is stated to be a hydrolysis product of the strong adhesive shellac.

The pure dyes, aurin and rosolic acid were tested because triphenyl carbinol had been found to be an excellent adhesive for metal and these two dyes are formed from the unstable, trihydroxy derivatives of triphenyl carbinol and tolyl diphenyl carbinol respectively. As expected they are good adhesives.* The constitution of these derivatives is similar to that of a probable Bakelite resin intermediate. The aurin had no sharp melting point and on strong heating gave an extremely viscous material. This appears to be of real significance and it is probable that with such adhesives as aurin, pitch, sulphur, etc. the liquid heated to the maximum viscosity gives

TABLE III

Tension tests (lbs./sq. in.) of joints made with pure substances between smooth metal test pieces

| | | | | |
|-----------------------------------------------|---------------|------------------|---------------|-----------------------|
| Cetyl alcohol** | Steel 120 | Nickel steel 130 | Aluminium 120 | 110 |
| | 100 | | | |
| Elaidic acid | Aluminium 130 | 120 | | |
| Cerotic acid | Steel 200 | Nickel steel 250 | Duralumin 250 | 200 |
| Stearic acid | Nickel 215 | 200 | 175 | 170 155 145 145 (120) |
| " " | Steel 210 | Nickel steel 190 | Duralumin 150 | 140 |
| " " | 110 | Copper 135 | 120 | 80 |
| Dihydroxystearic acid | Nickel 570 | 560 | 420 | 350 Steel 360(?) |
| " " | Duralumin 480 | 420 | 350 | Copper 335 215 |
| Cinnamic acid | Copper 300 | 250 | | |
| p-Nitraniline | Steel 250 | | | |
| β -Naphthol | Duralumin 250 | | | |
| Resorcin | Steel 250 | | | |
| Catechin | Steel 300 | | | |
| p-Toluidine | Aluminium 350 | 300 | | |
| Azelaic acid | Copper 500 | | | |
| Uric acid | Aluminium 700 | 600 | 600 | |
| Sulphur | Aluminium 900 | | | |
| Rosolic acid | Copper 900 | Steel 700 | | |
| Malachite Green G (Solid Green Crystals O) | Copper 870 | | | |
| Aurin | Aluminium 600 | 560 | 520 | 430 400 |
| " | Nickel 1000 | 960 | 900 | 640 320† |

* Aurin heated with glycerine gave a jelly on cooling.

** Static friction (Hardy) 0.1132 for steel on steel.

† Very thick film.

the optimum strength of joint. Such viscous molten adhesives are obviously capable of forming much stronger joints if only sufficient pressure were used to make the films really thin instead of unusually thick.

The numerical data are collected in Table III and to these may be added the following qualitative observations. Nitrazole and cerasine yellow were somewhat weak, tannin orange and china green weak, and thioflavine and azophor red so weak that they were easily broken by hand. Piperic acid, acenaphthene and tribromophenol gave weak joints with aluminium.

It may be mentioned that the tests in Table III include test pieces of Duralumin for the first time. From the rule observed in previous papers connecting joint strength and mechanical properties of metals it might be expected to give joints of strength lying between nickel and copper.

"Overheated" Glycollic Acid as a Strong Adhesive

The strongest commercial adhesives for metals are those prepared from shellac which probably has a lactide structure. Pure glycollic acid itself is a very poor adhesive for metals but glycollide can be prepared by "overheating" the glycollic acid. Our previous experience with saligenin and Rochelle salt (Proc. Roy. Soc., 113 A, 609 (1926)), had shown that heating such substances far above their melting points considerably increases their adhesive strength as adhesives. The expectations drawn from these considerations were confirmed by the following tests with two specimens of "overheated" glycollic acid.

Sample 1 was prepared by heating pure glycollic acid very gradually to 150° and maintaining it at that temperature for several hours, the whole operation taking about one day. A hard compact product was obtained on cooling. The remarkable strength of nearly one ton per sq. in. obtained with smooth nickel surfaces fully rivals that obtainable with many recognized adhesives. Sample 2 was prepared by heating the glycollic acid much more rapidly to 150° and the joints although strong did not equal those obtained with Sample 1.

TABLE IV

Tension tests (lbs./sq. in.) with "overheated" glycollic acid between smooth plane metal surfaces

| | |
|----------|--------------------------------------------------|
| Sample 1 | Nickel 2200 |
| Sample 2 | Steel 1600 Nickel 1350 Copper 1050 1000 |

In this connection it may be recalled that prolonged mechanical working of adhesives such as the waxes at not too high a temperature greatly enhances their adhesive power. Evidently the degree of orientation and aggregation of the molecules is affected thereby (see previous papers, loc. cit.)

Stability of Joints

The question of stability of various kinds of joints made with various adhesives is important both from a theoretical and a practical point of view. In a very recent discussion on Cohesion (Faraday Soc., 74, 53 (1928)) Desch has pointed out that the influence of the rate of application of stress on the

deformation produced by that stress in engineering materials deserves more attention than it has received hitherto. This is likewise our experience with glue and in many cases the mechanical properties of joints and of films of recognized adhesives as apart from the joints depend to an appreciable extent upon the rate of loading employed.⁶ However the extent of the influence of the rate of loading on the ultimate film or joint strength would appear to be very dependent on the nature of the adhesive. Indeed preliminary experiments with substances such as rosolic acid, malachite green, and "overheated" glycollic acid in which the joints were placed under continuous heavy loads (from $\frac{1}{2}$ to $\frac{2}{3}$ the final breaking load) for days, weeks, or a month without failure seem to indicate a much superior stability to that of the recognized adhesives. For example, "overheated" glycollic acid between smooth nickel surfaces held 760 lbs./sq. in. for a month and did not then break until the load was increased to 2200 lbs./sq. in. Rosolic acid with copper surfaces similarly showed no signs of failure in a week with a load $\frac{2}{3}$ the final breaking strength. A joint with malachite green between copper surfaces held 700 lbs./sq. in. for a day before being broken at 870 lbs./sq. in. Stearic acid between nickel surfaces held 140 lbs./sq. in. for five minutes being afterwards broken at 175 lbs./sq. in.

Pure Substances as Adhesives for Wood

Investigation of glued wooden joints has in the past presented much uncertainty both on account of the lack of quantitative concordance in the numerical values of even the most carefully repeated tests and on account of the divergent views held with regard to the nature and mechanism of the adhesion observed. Part of the trouble is due to the fact that, as we have shown, the film of glue is immensely stronger than the wood itself, and part would seem to be caused by the fact that the ordinary glue is applied as an aqueous solution from which most of the water must evaporate before the shrunken residue can hold the wood together. Entirely new possibilities of studying such joints, in which many of the uncertainties are replaced by definite controllable factors, are afforded by employing pure chemical substances instead of the aqueous solutions of glue.

There has been great uncertainty as to whether or not there is any specific adhesion of glue to the cellulose or lignin of the wood, or whether the whole or an important part of the observed adhesion may be due to merely mechanical embedding of the solidified glue in the microscopic and more particularly ultramicroscopic pores of the wood. We have found no definite evidence for the existence of any specific adhesion, and much for the mechanical effect. McBain and Hopkins⁷ found that sorption from an aqueous solution of glue is negative and that the amount of water taken up, as shown by blank experiments appears to preclude any simultaneous sorption of glue. It is a *non sequitur* to infer as Brown and Truax have done that because an aqueous solution of glue wets wood that the glue would likewise wet or adhere to the wood in the absence of water. We can however now adduce a clear case of a wooden joint which is partly specific and partly mechanical

when pure melted coumarin is allowed to solidify *in situ* between wooden surfaces using test pieces of walnut as described in our previous papers. The liquid coumarin does wet the wood. Such joints are a fifth as strong as those made with the best aeroplane propeller glue in spite of the fact that on account of the high melting point of coumarin (67°) the test pieces were warped and in no case was the coumarin film complete. Under such circumstances the highest breaking load on the shear test pieces was 1 ton. Only a few other preliminary observations may here be recorded. Thus azelaic acid and myricyl alcohol give fairly strong joints (over 50 lbs./sq. in.), whereas those made with cetyl alcohol and terpineol are very weak (less than 25 lbs./sq. in.), all in accordance with our experience with metals.

Summary

1. Pure chemical compounds of different types exhibit very different adhesive power when used for joining polished metal surfaces, the strength varying in definite relation to chemical constitution. The highest adhesive power was of the order of 1 ton/sq. in.

2. The rules derived from our previous studies with commercial adhesives are confirmed when using pure substances. For example, there is a notable increase of strength when the film of adhesive is made exceedingly thin, a phenomenon which we ascribe to chains of oriented molecules extending from the surfaces well into the liquid or solidified adhesive.

3. The intimate relation between the study of adhesion and of lubrication is well exemplified by the compounds investigated. Adhesive power goes parallel with static friction.

4. It is pointed out that the use of pure chemical compounds greatly simplifies the scientific study of wooden joints. Pure coumarin affords a good example of a strong joint in which both specific adhesion and mechanical embedding are operative.

References

- ¹ McBain and Lee: Proc. Roy. Soc., 113A, 605-620 (1926).
- ² Doubleday: J. Chem. Soc., 121, 2875 (1922).
- ³ Lee: Trans. Faraday Soc., 23, 634-40 (1927).
- ⁴ See McBain and Davis: J. Am. Chem. Soc., 49, 2230-54; McBain: Nature, 120, 362; McBain and Lee: J. Phys. Chem., 31, 1674-80 (1927).
- ⁵ See Harries and Nagel: Ber., 55 (B), 3833-48 (1922).
- ⁶ See Ind. Eng. Chem., 19, 1005-8 (1927).
- ⁷ McBain and Hopkins: J. Phys. Chem., 29, 188-204 (1925).

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EFFECT OF ALKALINITY ON BASIC CUPRIC SULFATES*

BY O. A. NELSON*

One needs only to review in a cursory manner the very voluminous literature on basic copper sulfates to notice considerable disagreement among the various investigators as to methods of preparation and composition of the products. In the case of the cupric compounds at least thirty are reported and described, in which the $\text{CuO}:\text{SO}_3$ ratio varies from 10:1 to 2:1, with varying amounts of water of hydration.

No attempt will be made to give a comprehensive résumé of the results of the scores of research men or technicians who have made observations on these products, from time to time since Proust¹ in 1800 prepared a bright green powder of the composition $4\text{CuO}\cdot\text{SO}_3\cdot 4\text{H}_2\text{O}$. Brief mention must, however, be made to a few of these in order to point out the evidence, or lack of evidence, for the assumption that the basic cupric sulfates are true chemical compounds.

S. U. Pickering² obtained a product whose analysis corresponded to the formula $10\text{CuO}\cdot\text{SO}_3$ by adding 1.8 mols of sodium hydroxide to a dilute solution of 1.0 mol cupric sulfate, the solution at this point becoming permanently alkaline to phenolphthalein. He observed that if less alkali were added, the precipitate showed a higher concentration of SO_3 , or the product was less basic. Thus adding only 1.5 mols the composition of the precipitate corresponded to the formula $4\text{CuO}\cdot\text{SO}_3$.

A product of the composition $8\text{CuO}\cdot\text{SO}_3$ was prepared by R. Kane³ by adding alkali to cupric sulfate solution and stopping short of the point at which the solution reacted alkaline. (Indicator not mentioned,—cochineal was possibly used, pH range 4.6 — 6.3). D. Smith⁴ could not duplicate Kane's results but obtained a precipitate to which he assigned the formula $6\text{CuO}\cdot\text{SO}_3$. Pickering² obtained a product of the composition $5\text{CuO}\cdot\text{SO}_3$, this time by adding only 1.60 mol base to 1.00 mol cupric sulfate.

Proust claimed that freshly prepared cupric hydroxide or carbonate passes into $7\text{CuO}\cdot 2\text{SO}_3\cdot 7\text{H}_2\text{O}$ when digested with a solution of cupric sulfate. This product was also obtained by Pickering² and others. Haberman⁵ prepared the hexahydrate of this product by dropping a concentrated solution of sodium carbonate into boiling cupric sulfate solution. A product of the composition $4\text{CuO}\cdot\text{SO}_3\cdot 4\text{H}_2\text{O}$ was first prepared by Proust¹ in 1800 and later by Field⁷ and Pickering² by the incomplete precipitation of cupric sulfate with potassium hydroxide. Sabatier⁸ found that if this product was treated with a saturated solution of cupric sulfate a compound was formed having the formula $5\text{CuO}\cdot 2\text{SO}_3\cdot 5\text{H}_2\text{O}$, but that this was unstable and passed into langite and cupric sulfate when treated with water. Bell and Taber⁹ failed

* Associate Chemist, Insecticide Division, Bureau of Chemistry and Soils. This work was done while the author was connected with the Insecticide and Fungicide Laboratory, Bureau of Chemistry, under the direction of Dr. C. C. McDonnell.

to confirm the existence of these two basic sulfates in their phase rule study of the system CuO , SO_3 and H_2O . Young and Stearn¹⁰ state that basic cupric sulfates are very probably "three component systems in which the components CuO , SO_3 and H_2O are continuously variable within certain limits."

Williamson¹¹ obtained results that could be expressed by the formula $(\text{CuO})_4 \cdot \text{SO}_3 \cdot 4\text{H}_2\text{O}$ but "more accurately by the improbable formula $(\text{CuO})_{19} (\text{SO}_3)_5 \cdot 18\text{H}_2\text{O}$." He considers the discrepancy between the two due to inadequate washing, error in analysis, or adsorbed copper sulfate, and that the former is most likely correct. Britton¹² titrated a solution of cupric sulfate with NaOH using an oxygen electrode and found 1.47 mol alkali per mol cupric sulfate necessary to render the solution neutral (pH.7), and concluded that the precipitate contains CuO and SO_3 in the ratio of 4 to 1.

According to A. H. Church¹³ and E. S. Larsen¹⁴ three different basic cupric sulfates are known to mineralogists under the names of antlerite, brochantite and langite. While the formulae assigned to these by different workers have varied somewhat, mineralogists are now agreed that they have definite compositions and refractive indices as follows:

| | | | | |
|------------------------------------------------------------------------|------------------|-----------------|------------------|--------------|
| Antlerite, $3\text{CuO} \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O}$ | $\alpha = 1.730$ | $\beta = 1.737$ | $\gamma = 1.785$ | orthorhombic |
| Brochantite, $4\text{CuO} \cdot \text{SO}_3 \cdot 3\text{H}_2\text{O}$ | $\alpha = 1.730$ | $\beta = 1.778$ | $\gamma = 1.803$ | " |
| Langite, $4\text{CuO} \cdot \text{SO}_3 \cdot 4\text{H}_2\text{O}$ | $\alpha = 1.708$ | $\beta = 1.760$ | $\gamma = 1.798$ | " |

These substances are well crystallized, and have well marked and quite distinctive optical properties as listed above and must be considered definite compounds.

Many more results might be considered, but these examples will indicate how indefinite and contradictory are the contributions on basic sulfates of copper. The reader is referred to Gmelin-Kraut's "Handbuch" and Mellor's "Comprehensive Treatise on Inorganic Chemistry," Vol. III, for more complete reviews of the literature on these products.

While the methods of preparing the various reported basic sulfates differed, a general comparison of these on the one hand with the resulting products on the other indicated that the basicity of the precipitate increased with the amount of base added to the copper salts. Pickering's, Sabatier's and Kane's results agree with this conclusion, as did also those of Young and Stearn.

In view of these observations it was thought possible to prepare a series of basic cupric sulfates in which it could be shown that the concentration of the SO_3 or the OH in the product was a continuous function of the ratio of the copper salts and alkali used in the preparation.

Method of Procedure

The method was somewhat similar to that used by Miller¹⁵ in his work on basic aluminum sulfates. A half molar solution of cupric sulfate was prepared and kept as a stock solution. A stock solution of exactly molar carbon dioxide free sodium hydroxide was also prepared and kept in a tightly stoppered bottle to prevent absorption of carbon dioxide from the air. 20 or 40 cc. of the

copper solution was used in each experiment, but before the addition of alkali these portions were diluted to 1 or 2 liters respectively thus making the concentration 0.01 molar. The base was also diluted to the equivalent concentration, and both solutions were cooled to below 5°C before bringing them together.

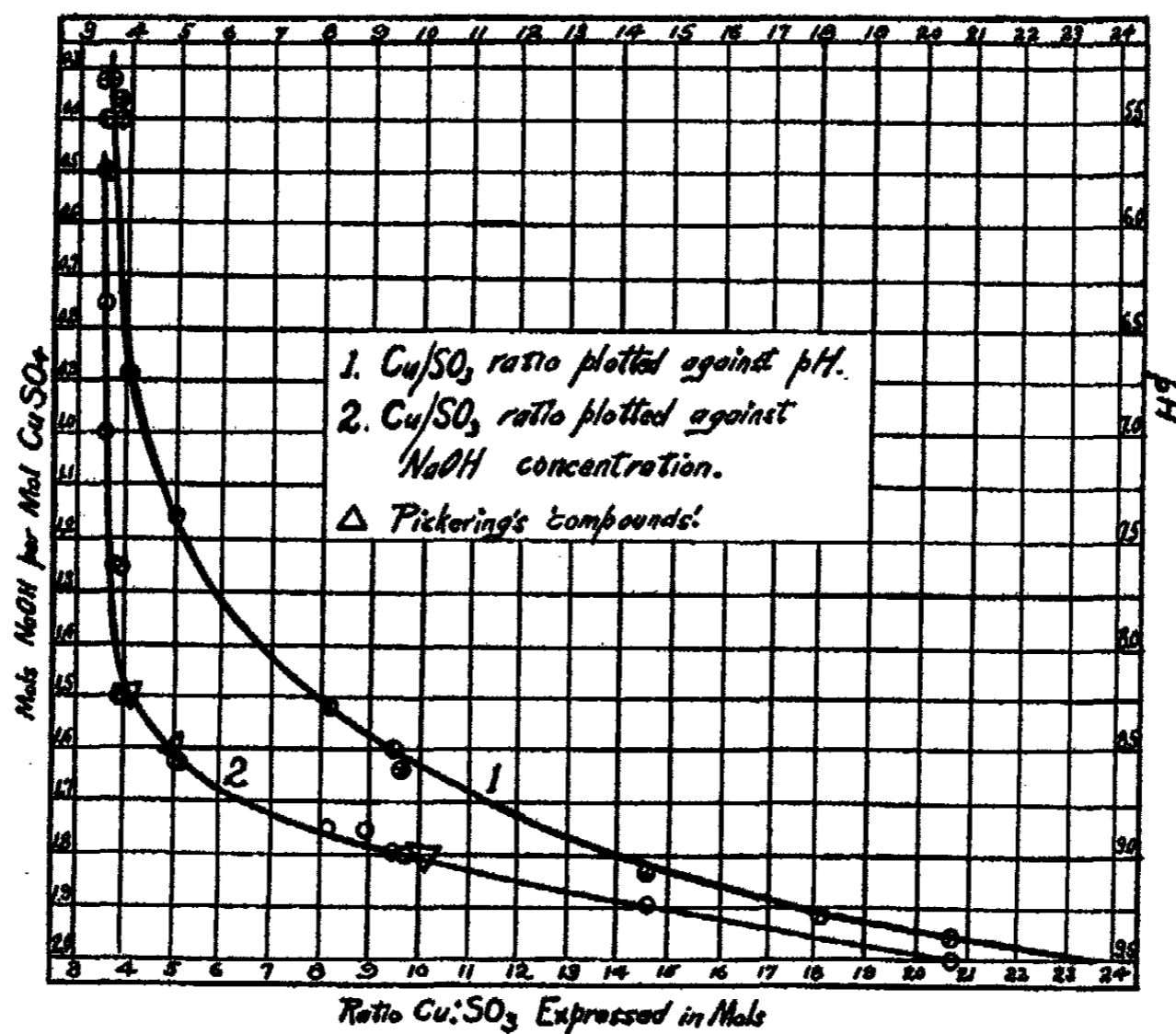


FIG. 1

The temperature was kept between 0° and 5°C until the stirring was discontinued. If the temperature rose much above this maximum the formation of copper oxide was hastened in the case of the more basic products, and this was to be avoided until washing free from alkali sulfates.

The sodium hydroxide was added to the cupric sulfate solution while the latter was stirred violently. The stirring was then continued for about two hours, and in some experiments the precipitates were allowed to remain in the mother liquor over night or longer. It was observed, however, that no changes in the composition of the precipitates took place when they were left in the mother liquor for long periods of time, thus indicating that equilibrium had been reached during stirring.* In runs where the pH value was over 7.0 stirring was accomplished by passing a current of carbon dioxide

* Since this paper was written, the author had occasion to prepare one or two more samples. These were left in the mother liquor for about two months, but on subsequent analysis showed the same composition within limits of error as did the ones used in this publication.

free air through the solution, or in a bottle out of contact with air to prevent the absorption of carbon dioxide. The flocculent precipitates were then allowed to settle, and samples of the supernatant liquids used for determination of hydrogen ion concentration by the colorimetric method.¹⁶ The precipitates were washed by decantation until no tests for sulfates in the washings were obtained with barium chloride.

The copper was determined in the precipitates by the electrolytic method, and the sulfate by the usual method, that of weighing as barium sulfate.

Table I gives the results obtained with different proportions of base added to cupric sulfate.

| Expt. No | Mols NaOH per Mol CuSO ₄ | pH Liquid | Weight in Portions analyzed Copper Grams | SO ₄ Grams | Ratio Cu/SO ₄ Molar |
|----------|-------------------------------------|-----------|------------------------------------------|-----------------------|--------------------------------|
| 9 | 0.50 | 5.3 | 0.1090 | 0.0474 | 3.40 |
| 9' | 0.50 | — | 0.1112 | 0.0460 | 3.60 |
| 10 | 0.75 | 5.5 | 0.1794 | 0.0771 | 3.50 |
| 2A | 1.00 | 5.3 | 0.2835 | 0.1223 | 3.51 |
| 2A' | 1.00 | 5.1 | 0.3284 | 0.1366 | 3.63 |
| 11 | 1.25 | 5.5 | 0.1641 | 0.0649 | 3.83 |
| 11' | 1.25 | 5.4 | 0.1649 | 0.0661 | 3.77 |
| 4A | 1.50 | 6.7 | 0.3213 | 0.0888 | 3.95 |
| 4A' | 1.50 | 6.7 | 0.2014 | 0.0768 | 3.97 |
| 12 | 1.625 | 7.4 | 0.1699 | 0.0512 | 5.01 |
| 12' | 1.625 | — | 0.1629 | 0.0477 | 5.16 |
| 13 | 1.75 | 8.3 | 0.1960 | 0.0363 | 8.16 |
| 7A' | 1.75 | — | 0.1507 | 0.0255 | 8.98 |
| 8A | 1.80 | 8.6 | 0.2380 | 0.0369 | 9.63 |
| 14 | 1.80 | 8.5 | 0.1924 | 0.0306 | 9.51 |
| 14' | 1.80 | — | 0.2044 | 0.0323 | 9.56 |
| 15 | 1.90 | 9.1 | 0.2066 | 0.0211 | 14.56 |
| 3A | 2.00 | 9.3 | 0.2393 | 0.0273 | 18.19 |
| 3A' | 2.00 | 9.4 | 0.2270 | 0.0166 | 20.73 |

Plotting these results on coordinate paper, curves were obtained that did not show a series of distinct breaks, as would be expected if a number of true chemical compounds had been formed. It was stated above that a product of the composition $4\text{CuO}\cdot\text{SO}_3\cdot 4\text{H}_2\text{O}$ had been obtained by a number of investigators. Referring to Table I and also to the Graph, curve 2, it will be seen that the condition for the formation of a product containing CuO and SO₃ in the ratio of 4 to 1 prevails only for experiments 4A and 4A' where exactly 1.5 mol base was added to one mol cupric sulfate solution. The results obtained, therefore, do not verify the existence of a compound such as the one suggested by Pickering and others but rather point to a product of fairly constant composition, in which the Cu/SO₃ ratio is about 3.5 to 1.0.

This agrees well with the formula suggested for the compound prepared by Proust under similar conditions. The experimental error at this end of the curve is very small, thus rendering it improbable that the variation from the points corresponding to the compounds of Cu/SO₃ ratio of 24:1 or 3:1 is due to such error.

It was stated in the first paragraph of this paper that a large number of basic cupric sulfates had been prepared and described. The different investigators have in nearly every case assigned definite formulae, including water of hydration, to the products obtained. The results given here do not appear to confirm the existence of many such basic cupric sulfates, but suggest rather that the numerous products reported in the literature are two or three component systems. The product represented by the vertical portion of curve 2 has an approximate formula of 7CuO.2SO₃. This therefore lies between the formula for antlerite and brochantite. The constancy of the composition of this product, over a fairly wide range of concentrations is indicative of it being a true chemical compound. It may well be that this is relatively unstable and if allowed enough time would go over into stable minerals known to mineralogists. In nature these minerals can form slowly, and their constituent atoms are able to take definite positions in the space lattice, but when deposition occurs rapidly as in the laboratory procedure herein described this apparently does not occur. Instead an amorphous precipitate forms, and in this the ratio of the constituents may not be the same as in the crystalline forms.

Table I shows that the pH is nearly constant until the Cu/SO₃ ratio begins to change rapidly with increasing hydroxide concentration. This would point to a compound formation, and also that if a compound had actually formed, it was unstable toward bases.

It will thus be seen that any product with a Cu/SO₃ ratio of 3.5 to 1.0 or over may be prepared by the addition of the proper quantity of base. Points representing the compounds suggested by Pickering have been included in the Graph, in order to show the close agreement between these and the products obtained in this work.

All precipitates were flocculent and when filtered became gelatinous, retaining such large quantities of water that any attempts at determining the water of hydration by chemical methods would obviously be futile.

It was also observed that as more alkali was added to the cupric sulfate solution the resulting precipitate contained less sulfate and more base, indicating formation of cupric hydroxide. For the lower part of the curve a solid solution suggests itself, although the data at hand are not sufficient to indicate conclusively whether we are dealing with a physical mixture or a solid solution.

These observations indicate then that the composition of basic cupric sulfates as prepared in the laboratory is dependent on the methods of preparation and the ratio between the reacting substances. In this respect the basic cupric sulphate behaved almost exactly like the basic aluminum sulfates, prepared by Miller. Miller found that the composition of basic aluminum sulfates remained approximately constant until a certain quantity of alkali

had been added. But on further addition of hydroxide the Al/SO₃ ratio changed very rapidly. This is exactly what the curves and table given here show regarding basic cupric sulfates.

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THE NATURE OF PRUSSIAN BLUE

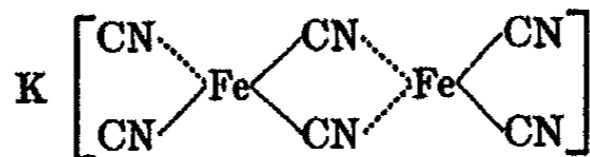
BY DAVID DAVIDSON AND LARS A. WELO

We owe our knowledge of the constitution of Prussian Blue largely to the work of Erich Müller and his students¹, whose results may be summarized as follows: There is an equilibrium in solution between ferric and ferrocyanide ions on the one hand and ferrous and ferricyanide ions on the other.

Soluble Prussian Blue is potassium ferric ferrocyanide, $KFe[Fe(CN)_6]$. It is obtained from equivalents of ferric chloride and potassium ferrocyanide or from equivalents of ferrous chloride and potassium ferricyanide. Insoluble

Prussian Blue is ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, in which the potassium of the soluble blue is replaced by ferric ion. Turnbull's Blue is made up of three molecules of the soluble blue in which two of the potassium atoms have been replaced by ferrous iron, hence $KFe[Fe[Fe(CN)_6]]_3$ or $KFeFe_2[Fe(CN)_6]_3$.

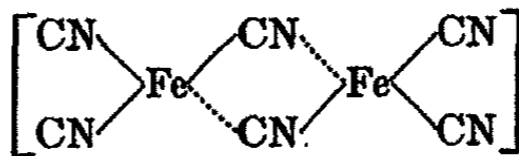
Recently, Reihlen and Zimmerman² have proposed a constitutional formula for Soluble Prussian Blue in which the two iron atoms are combined in the form of a complex polynuclear ion, thus:



Cambi³ has proposed a similar formula. No experimental evidence, however, has been advanced in support of such a structure. The present paper deals with the results obtained in the attempt to distinguish between the simple and the more complex structures. Neither the conductivity measurements in solution nor the magnetic measurements in the solid state have produced any evidence of the existence of the postulated polynuclear ion.

Conductivity Measurements

As may be seen from the corresponding formulae, Reihlen and Zimmerman's structure would yield only two ions in solution, whereas the simple formula indicates the occurrence of three. Since the insolubility of Soluble Prussian Blue⁴ renders conductivity measurements impracticable, attention was directed to the closely related ferric ferricyanide, $Fe[Fe(CN)_6]$, which is obtained by treating ferric chloride with potassium ferricyanide. Applying the ideas of Reihlen and Zimmerman to this compound, its structure becomes:



* From the Laboratories of the Rockefeller Institute for Medical Research, New York.

That is to say, while according to the simpler formulation, ferric ferricyanide appears to be a binary electrolyte, according to the second formulation it is manifestly a non-electrolyte. It is actually found, however, that a mixture of ferric alum and potassium ferricyanide solutions has a conductivity only slightly less than that of the component solutions and much greater than that of an equivalent amount of potassium and ammonium sulphates. The specific conductances are given in Table I.

TABLE I
Specific Conductances at 25°

| | |
|------------------------------------------------------------|---------------|
| 0.1 M $K_3Fe(CN)_6$ | 0.00393 Mhos. |
| 0.1 M $NH_4Fe(SO_4)_2 \cdot 12 H_2O$ | 0.00310 " |
| 0.2 M $K_3Fe(CN)_6$ + 0.2 M $NH_4Fe(SO_4)_2 \cdot 12 H_2O$ | 0.00645 " |
| 0.3 M K_2SO_4 + 0.1 M $(NH_4)_2SO_4$ | 0.00480 " |

Magnetic Measurements

Many simple ferric salts, such as $FeCl_3$, $Fe_2(SO_4)_3$, etc., have been extensively studied. For the purpose of the present paper it is only necessary to state that, in general, solid paramagnetics obey the generalized Curie law. $K_a(T - \Theta) = C_a$; that is, $1/K_a = (1/C_a)(T - \Theta)$ where K_a is the susceptibility per gram atom of the paramagnetic ion, T is the absolute temperature on the centigrade scale, Θ is a constant related to the molecular field, and C_a is the Curie constant referred to the gram atom. But the constants C_a (reciprocal of the slope) and Θ (intercept on the temperature axis) take different values according to the temperature range. The curve showing $1/K_a$ plotted against T consists generally of a series of straight lines with well-defined breaks if the range of temperatures is great enough and if the points are close enough together. We have made a close study of the observations for all of the six ferric salts measured by Ishiwara⁶ and Honda and Ishiwara⁶, and the ferric sulphates measured by Théodoridès⁷ and by Onnes and Oosterhuis⁸, in order to determine the range of values of C_a to be expected in any iron

TABLE II
Résumé of Magnetic Data on Ferric Salts in the Solid State

| Salt | Curie constant, C_a . | Corresponding number of Weiss magnetons, P. | Authors |
|-----------------------------|-------------------------|---------------------------------------------|-------------------------|
| $FeCl_3$ | 3.80, 4.08 | 27.4, 28.4 | Ishiwara, and |
| $FeCl_2(NH_4Cl) + H_2O$ | 3.98, 4.29, 5.30 | 28.0, 29.1, 32.4 | Honda and |
| $\frac{1}{2}[Fe_2(SO_4)_3]$ | 3.85, 4.22, 4.71 | 27.6, 28.9, 30.5 | Ishiwara |
| $NH_4Fe(SO_4)_2 + 12 H_2O$ | 4.43 | 29.6 | |
| $NH_4Fe(SO_4)_2$ | 3.94, 4.08, 4.14 | 27.9, 28.4, 28.6 | |
| $Fe(C_5H_7O_2)_3$ | 3.92, 4.51, 4.81 | 27.9, 29.8, 30.8 | |
| $\frac{1}{2}[Fe_2(SO_4)_3]$ | 4.233, 4.245 | 28.93, 28.97 | Théodoridès |
| $NH_4Fe(SO_4)_2 + 12 H_2O$ | 4.26 | 29.0 | Onnes and Oosterhuis |

salt giving the simple ion⁹ Fe^{+++} . They appear in Table II. Values calculated from doubtful line segments were rejected. Values of the constant Θ are not shown as we are not concerned about them in this paper. Following common practice we include corresponding values for the Weiss magneton number calculated by the formula $P = \frac{\sqrt{3 R C_a}}{1123.5} = 14.07 \sqrt{C_a}$, the gas constant R being 83.15×10^6 .

The ferrocyanides have long been known to be diamagnetic. We have measured the susceptibilities of the ferrocyanides of hydrogen, potassium, sodium, and calcium in the attempt to evaluate the gram atomic susceptibilities of the iron in them. The results appear in Table III, where

K = specific susceptibility.

K_m = molecular susceptibility.

K_a = gram atomic susceptibility.

K_d = sum of gram atomic susceptibilities of constituents other than iron.

TABLE III

Magnetic Data on the Ferrocyanides

| Ferrocyanide | Molecular weight | Magnetic Data | | | | Mean $K_a \times 10^6$ |
|----------------------------------------------------------------|------------------|-----------------|-------------------|-------------------|-------------------|------------------------|
| | | $K \times 10^6$ | $K_m \times 10^6$ | $K_d \times 10^6$ | $K_a \times 10^6$ | |
| $\text{H}_4[\text{Fe}(\text{CN})_6]$ | 216 | -0.328 ± 3 | -70.8 | -75.8 | +5.0 | |
| $\text{K}_4[\text{Fe}(\text{CN})_6] + 3\text{H}_2\text{O}$ | 422 | -0.408 ± 2 | -172.2 | -177.2 | +5.0 | |
| $\text{Na}_4[\text{Fe}(\text{CN})_6] + 9.5\text{H}_2\text{O}$ | 475 | -0.474 ± 3 | -225.0 | -224.0 | -1.0 | |
| $\text{Ca}_2[\text{Fe}(\text{CN})_6] + 10.5\text{H}_2\text{O}$ | 481 | -0.465 ± 1 | -223.5 | -231.8 | +8.3 | +4.3 |

To calculate the values of K_d shown in the table, the following gram atomic susceptibilities given by Pascal¹⁰ were adopted: $\text{H} = -2.9 \times 10^{-6}$, $\text{K} = -18.5 \times 10^{-6}$, $\text{Na} = -9.2 \times 10^{-6}$, $\text{Ca} = -15.8 \times 10^{-6}$, $\text{C} = -6 \times 10^{-6}$, $\text{N} = -5.5 \times 10^{-6}$, $\text{H}_2\text{O} = -13.0 \times 10^{-6}$, and the correction $+0.8 \times 10^{-6}$ for each of the CN groups.

As the table shows, the mean of the four values of the iron atomic susceptibilities is $K_a = +4.3 \times 10^{-6}$. It is to be expected that the individual values of K_a should fluctuate considerably because of experimental errors in K and because of doubt that Pascal's diamagnetic constants are strictly applicable to these compounds. Errors in the determination of K_a for iron in the ferrocyanides are of no importance in connection with the subject of this paper. Here we are concerned with Prussian Blues having one or more ferric ions per molecule, each having an atomic susceptibility of the order 14000×10^{-6} to 21000×10^{-6} within the range of temperature used. The paramagnetic contribution of iron, if any, in the ion $\text{Fe}(\text{CN})_6$ is itself entirely negligible.

The magnetic properties of soluble and insoluble Prussian Blue as they have been formulated in the foregoing discussion can now be predicted. Soluble Prussian Blue, $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$, should behave as a double potassium ferric salt of hydroferrocyanic acid in which all of the paramagnetism is due

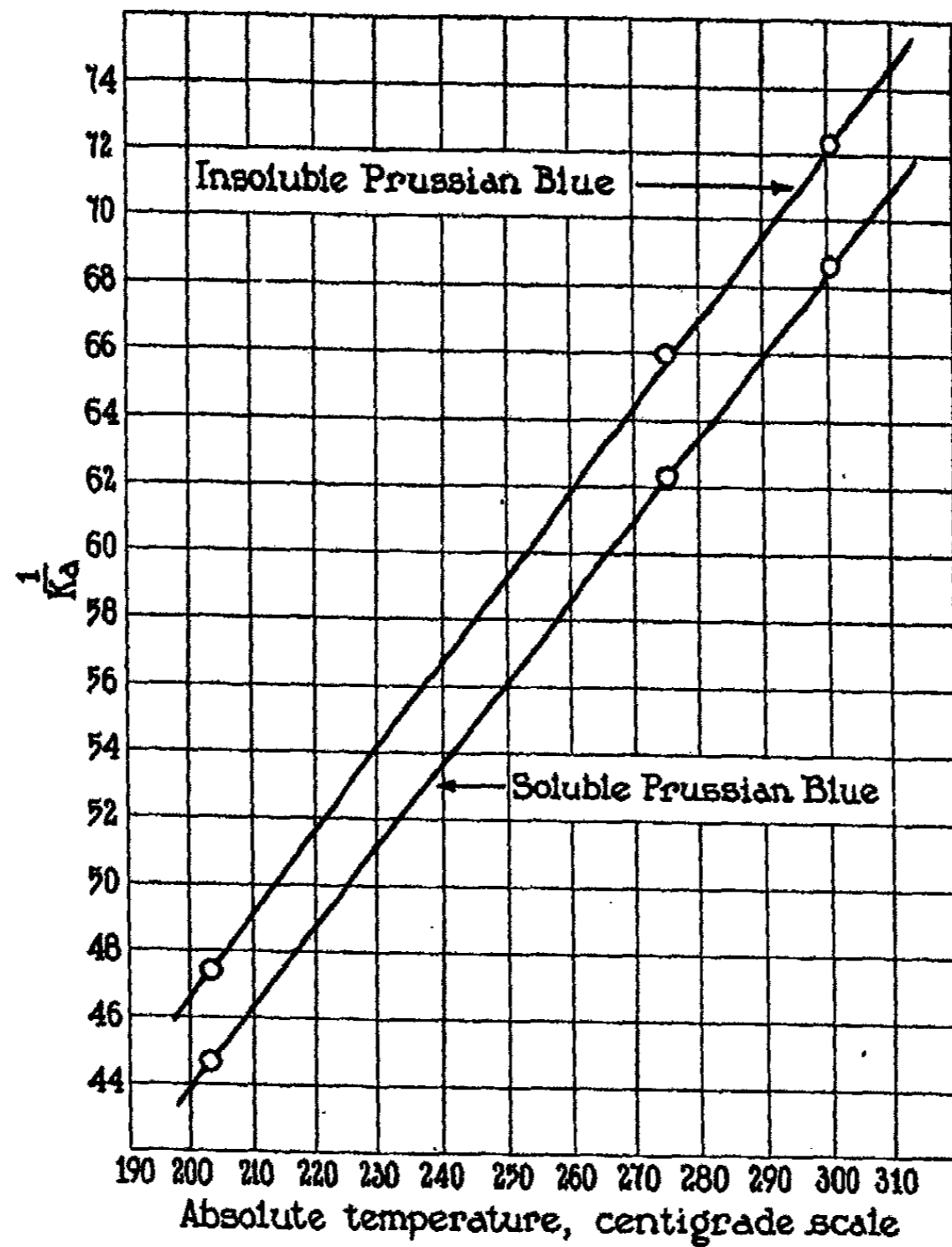


FIG. 1

+++
to the ion Fe^{III} . The Curie constant should be, according to Table II, not less than 3.80 and might be as high as 5.30. In the insoluble Prussian Blue, $\text{Fe}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$, only four of the seven iron atoms per molecule play a part in the paramagnetism. We may assume that each of the four contributes equally. We should obtain again, for each ferric ion, a Curie constant within the limits 3.80 and 5.30. The corresponding limits of the Weiss magneton numbers should be 27.4 to 32.4.

Each Prussian Blue was measured at three temperatures: that of the room; when surrounded by melting ice, giving a final temperature of 2.1°C ; and when surrounded by solid CO_2 , giving a temperature of -70°C . These are sufficient in number and extend over a large enough range to determine whether or not the Curie law is obeyed, and, if so, to enable us to determine the constant C_a and if we so desire, Θ . The results are shown in Table IV and in Fig. 1. The meaning of the symbols T , K , K_m , K_d , and K_a , has already been stated. N is the number of iron atoms per molecule assumed to be responsible for paramagnetism and K_M is the molecular susceptibility K_m corrected for diamagnetism and for the small positive residual of iron in $\text{Fe}(\text{CN})_6$ by subtracting the quantities K_d . As shown in the figure, the relation between $1/K_a$ and T is accurately linear for each of the Prussian Blues throughout the range studied and in accord with the Curie law which may be written in the form, $1/K_a = (1/C_a)(T - \Theta)$. The Curie constant C_a can be determined from any two points on the line by the formula, $C_a = \frac{T_1 - T_2}{1/K_{a1} - 1/K_{a2}}$ and, similarly, $\Theta = \frac{T_2 K_{a2} - T_1 K_{a1}}{K_{a2} - K_{a1}}$.

TABLE IV
Magnetic Data on Prussian Blues

| Prussian Blue | Mole- cular weight | N | T | $K \times 10^6$ | $K_m \times 10^6$ | $K_d \times 10^6$ | $K_M \times 10^6$ | $K_a \times 10^6$ | $\frac{1}{K_a}$ |
|-----------------------------------------|--------------------------|---|-------|-----------------|-------------------|-------------------|-------------------|-------------------|-----------------|
| Soluble | | | 300.5 | 42.45 | 14460 | -103 | 14563 | 14563 | 68.68 |
| $\text{KFe}[\text{Fe}(\text{CN})_6]$ | 341 | 1 | 275.2 | 46.73 | 15940 | -103 | 16043 | 16043 | 62.32 |
| + $1.9\text{H}_2\text{O}$ | | | 203.1 | 65.40 | 22290 | -103 | 22393 | 22393 | 44.70 |
| Insoluble | | | 300.6 | 49.05 | 55000 | -368 | 55368 | 13842 | 72.35 |
| $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ | 1120 | 4 | 275.2 | 53.75 | 60250 | -368 | 60618 | 15154 | 66.00 |
| + $14.5\text{H}_2\text{O}$ | | | 203.1 | 75.00 | 84000 | -368 | 84368 | 21092 | 47.40 |

It is convenient to take the values of T and $1/K_a$ from the graph.

1. Soluble Prussian Blue.

$$\text{When } T_1 = 300, \frac{1}{K_{a1}} = 68.60.$$

$$T_2 = 200, \frac{1}{K_{a2}} = 43.90.$$

$$C_a = \frac{300 - 200}{68.60 - 43.90} = \frac{100}{24.70} = 4.05.$$

Giving for the magneton number,

$$P = 14.07\sqrt{4.05} = 28.3.$$

For Soluble Prussian Blue, $\Theta = +22$.

2. Insoluble Prussian Blue.

$$\text{When } T_1 = 300, \frac{1}{K_{a1}} = 72.20.$$

$$T_2 = 200, \frac{1}{K_{a2}} = 46.70.$$

$$C_a = \frac{300 - 200}{72.20 - 46.70} = \frac{100}{25.5} = 3.92.$$

$$\text{Giving } P = 14.07\sqrt{3.92} = 27.8.$$

For Insoluble Prussian Blue, $\Theta = +14.7$.

We see, then, that the treatment of the magnetic data demanded by the formulations $\text{KFe}[\text{Fe}(\text{CN})_6]$ and $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ for soluble and insoluble Prussian Blue, respectively, leads to the Curie constants 4.05 and 3.92 and the magneton numbers 28.3 and 27.8 which are within the permissible limits for ferric ions, according to Table II.

It is of interest to treat the magnetic data on the basis of the alternative formulations as polynuclear compounds: $\text{K}[\text{Fe}_2(\text{CN})_6]$ and $\text{Fe}[\text{Fe}_2(\text{CN})_6]_3$. In the case of the soluble Blue we must assume that each iron atom in the ion $\text{Fe}_2(\text{CN})_6$ plays the same part and contributes half the total. The Curie constant per gram atom of iron,

$$C_a = \frac{4.05}{2} = 2.025$$

and the magneton number,

$$P = 14.07\sqrt{2.025} = 20.0$$

These values of C_a and P have never hitherto been observed in any salt of iron.

In the case of the insoluble Blue the measured value of the Curie constant, referred to the grain molecule, is

$$C_M = 4 \times 3.92 = 15.68$$

From our measurements on soluble Blue, the contribution of each ion $\text{Fe}_2(\text{CN})_6$ is 4.05 and for the three ions $\text{Fe}_2(\text{CN})_6$ in the formulation $\text{Fe}[\text{Fe}_2(\text{CN})_6]_3$, $3 \times 4.05 = 12.15$. The Curie constant C_a referred to the ion Fe^{+++} becomes

$$C_a = 15.68 - 12.15 = 3.53$$

and the magneton number,

$$P = 14.07\sqrt{3.53} = 26.4$$

These values of C_a and P are, indeed, observed in iron salts, but they are characteristic of the ferrous ion in ferrous salts and not of the ferric ion re-

quired by the formula $\text{Fe}[\text{Fe}_2(\text{CN})_6]_3$. In both the soluble and the insoluble Blue, therefore, the formulations as polynuclear compounds are inconsistent with the known magnetic properties of iron salts

The authors are indebted to Dr. Oskar Baudisch to whom their interest in the subject is due and to Dr. P. G. Colin who very kindly made the conductivity measurements.

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December 22, 1927.

THE INFLUENCE OF PRESSURE ON THE HIGH-LOW INVERSION OF QUARTZ

BY R. E. GIBSON

Introduction

When a crystal of quartz is heated to temperatures slightly over 400° its properties such as volume, heat capacity, crystal angles and refractive indices vary much more rapidly with temperature than do those of most other substances. Indeed, Wright¹ has pointed out that the variation of the crystal angles of quartz is an exponential function of the temperature above 500° . White² observed that the rise in the heat capacity was not entirely explained by the volume changes. It seemed that heat necessary for a coming change was being absorbed and White called the excess heat capacity a "distributed latent heat." These changes just mentioned proceed at an increasing rate until at 573° a catastrophic transformation occurs and the trigonal or low quartz is converted to the hexagonal or high form.

Many investigations³ have been made to determine the exact temperature of this transition point. Recently, Bates and Phelps⁴ placed it at 573.3° for the low→high inversion and 572.4° for the high→low inversion. Their experiments being of a very high order of accuracy and being made on blocks of quartz have brought to light several important facts. Chief among these is the fact that during the low→high inversion the temperature of the block falls, though the temperature of the furnace is slowly rising or is held stationary. Furthermore, this drop in temperature is constant for many specimens and various rates of heating. It is about half a degree. They also observed that the speed of the reaction was very high and that all attempts to check the reaction, once it had started, were futile. Clearly we are dealing with a curious type of phase change and one which must be more fully studied before it is classed with such phenomena as melting or the inversion of a substance like tin.

The high-low inversion of quartz is, moreover, of interest to geologists. Wright and Larsen⁵ showed that from an optical and crystallographic study it is possible to infer with fair probability whether a piece of quartz has ever been at a temperature above the high-low inversion point. It is, therefore, possible in some cases to place an upper limit to the temperature at which quartz and minerals associated with it were formed. It was, of course, recognized that under the pressures existing at depths in the earth, quartz would invert at a higher temperature than at one atmosphere pressure and

¹ F. E. Wright: *J. Wash. Acad. Sci.*, 3, 485-494 (1913).

² W. P. White: *Am. J. Sci.*, 47, 1-43 (1919).

³ See R. B. Sosman: "The Properties of Silica," p. 119 (1927).

⁴ *Bur. Standards Sci. Papers*, (No. 557) 22, 315 (1927).

⁵ *Am. J. Sci.*, 27, 421-447 (1909).

that unless some idea of the magnitude of this change were available the above method would be only approximate. Assuming that we are dealing with a change to which the Clausius-Clapeyron equation may be applied, we should be able to calculate the influence of pressure on this inversion from heat and volume data. Unfortunately, reliable data of this nature are not available. Day, Sosman and Hostetter¹ made accurate determinations of the density of quartz from room temperature to 1000°. In the vicinity of 500°–570° the volume-temperature curve shows a distinct rounding similar to the effect already described and leaves some doubt as to what is to be taken as the volume change on inversion. There is, however, a sharp instantaneous change equal to 3.25 cc. per kg. at 575° or so. This we will call the "instantaneous volume change" and use it later. In the case of the heat change there is added to this difficulty the fact that the data are fragmentary and rather inconsistent—which is not surprising when the experimental difficulties are considered.

Table I shows the calculated rise of the inversion point for 1000 megabaryes,² which corresponds to various estimates of the latent heat.³ It will be seen at once that the best data give values for the inversion at 1000 megabaryes (corresponding to a depth of approximately 3 km in the earth) varying by 23°C. Hence for geophysical purposes a direct determination of the effect of pressure on the high-low inversion is desirable.

TABLE I
Heat and Volume Data for the High-Low Inversion of Quartz

| Volume change cc. per kg | Heat change cal. per kg | Rise of Inversion Temp. for 1000 megabaryes | Author and Notes |
|-----------------------------|----------------------------|---------------------------------------------------|---------------------------------|
| 3.25 | 2500 | 26.3 | Sosman (most probable estimate) |
| 3.25 | 4300 | 15.3 | White (1919) |
| 3.25 | 1700 | 38.7 | White (Sosman's estimate) |
| 3.25 | 4200 | 15.7 | Cohn (Norwegian Quartz) |
| 3.25 | 4100 | 16.1 | Cohn (Rose Quartz) |
| 3.25 | 4100 | 16.1 | Cohn (Hohenbocka Sand) |

Scope of Paper. In this paper I propose to give the results of determinations of the temperature of the high-low inversion of quartz under various uniform hydrostatic pressures from one to three thousand megabaryes and so obtain the rise in inversion temperature as a function of the pressure. From this I shall calculate the latent heat of inversion.

Materials. In preliminary experiments powdered quartz was used. This came from the Baker and Adamson Chemical Company.

¹ Am. J. Sci., 37, 1-39 (1914).

² 1 megabarye = 10^6 dynes/cm² = 0.987 atmosphere.

³ Sosman: Op. cit., p. 322.

For the major part of the work, however, a small block of quartz was employed. This was cut from a well-formed flawless crystal of quartz which came from Hot Springs, Arkansas. It was given me by Dr. Foshag at the U. S. National Museum and was marked with the number 83660.

Experimental

Apparatus. The bomb or vessel in which the pressure was generated was designed by Dr. L. H. Adams, built by Mr. Jost of this Laboratory, and was similar to that described by Smyth and Adams.¹ It differed from theirs in dimensions.

The apparatus is shown diagrammatically in Fig. 1. It consists essentially of a steel cylinder J_1 grooved spirally on the outside. On this inner wall is shrunk an outer wall J_2 which is made of hardened vanadium steel and is the chief pressure-resisting agency.

In the spiral grooves G between these two walls flows hot water which serves to conduct away any surplus heat and prevents the outer jacket from becoming excessively hot. The ends of the cylinder are closed by two lids L_1 and L_2 , the joints being made gas tight by copper gaskets at A . Each lid is made in two sections, as shown, and cooling water flows in the two concentric channels W_1 and W_2 .

Inside the bomb is an electric furnace F , made of two coils of platinum wire wound on coaxial alundum tubes. The lower part of the furnace is filled by the baffles B . The space between the heating coils and the walls is filled with alundum sand.

The thermocouple leads T_1, T_2, T_3 pass through the lid as illustrated. The packings TP are made from soapstone which is cut and bored to fit and is flowed into place by the application of a high differential pressure. The furnace leads of which one is shown at H are also packed in the same way. The lids are held on by an oil press which is capable of a force of 500 tons. This method is very satisfactory, as for each internal pressure a requisite force from

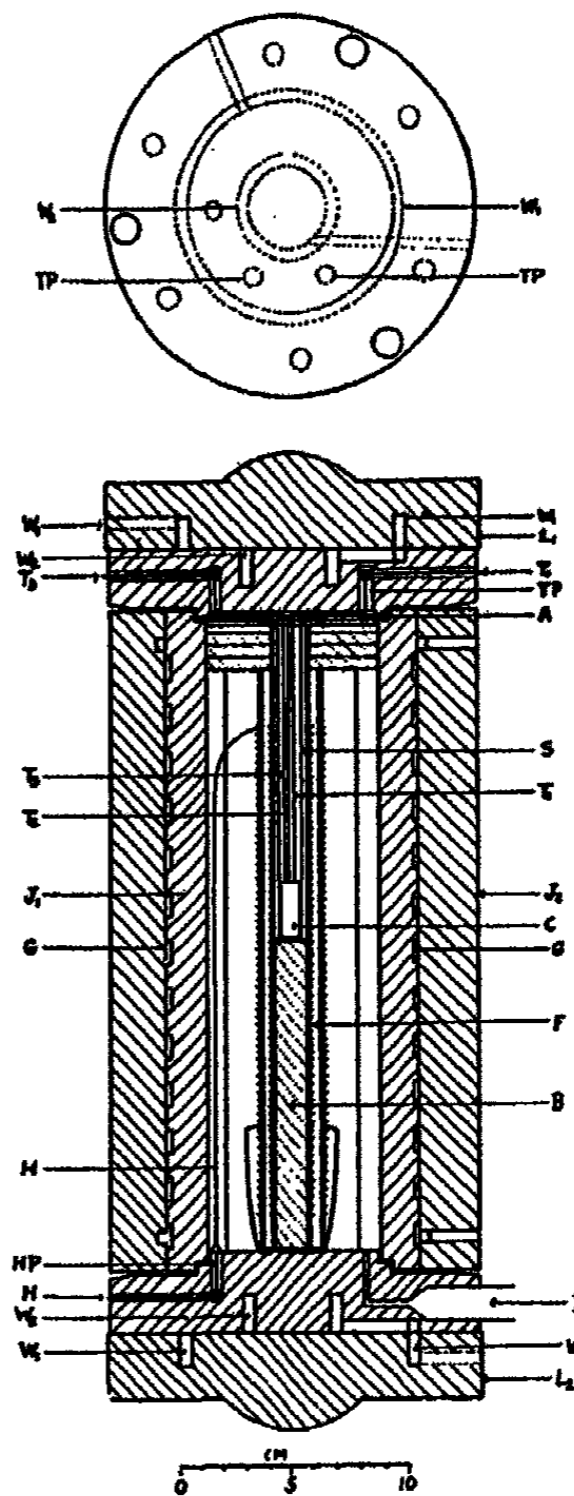


FIG. 1
Diagrammatic sketch of high temperature bomb.

¹ J. Am. Chem. Soc., 45, 1172 (1923).

the press can be exerted to balance the pressure on the lids and so no unnecessary strains are set up in the material of the bomb.

To generate pressure inside the vessel an appropriate amount of liquid carbon dioxide, carefully dried, is introduced at *I* from a pump. The system is closed off by a control valve and the heating current is switched on.

As the inversion point was detected by its heat effect, it was absolutely essential to obtain reasonably steady thermal conditions in the bomb. The introduction of the large amounts of gas necessary for generating the pressures used caused several disturbances which had to be eliminated before any results at all could be obtained. These disturbances were of three kinds:

- (1) Convection currents
- (2) Vertical temperature gradients
- (3) Change of position of the spot of maximum temperature in the furnace.

Convection currents played havoc with temperature readings, as will be readily understood from a glance at the apparatus. In the bomb there is a very dense gas at a temperature of 600° in the center and 100° at the ends. Disturbances of this kind were removed by filling up the furnace with as much solid material as possible. The silica glass tube *S* was wrapped with asbestos string on the outside so that it fitted tightly into the furnace. The crucible *C* was made to slide neatly into *S* and the space between *C* and the upper lid of the bomb was filled with alundum discs bored to take the thermel leads. These discs are not shown in the diagram. As alundum conducts electricity appreciably at high temperatures, the thermocouple wires were insulated with fine silica glass tubes. By this simple method the convection disturbances were cut down to a minimum.

Temperature gradients presented a more difficult problem, and one which was never completely solved. The bomb was explored by means of two thermocouples spaced vertically 1.5 cm apart. A fairly quantitative idea of the temperature gradients at different levels in the bomb and at the various temperatures and pressures was obtained. At no spot was the gradient entirely satisfactory and at the level where the quartz was placed it amounted to 4° per cm. As the quartz block was 1 cm high this state of affairs was unsatisfactory (1) because it led to faulty readings on the thermocouple, and (2) it caused shattering of the specimen. A method of reducing still further the temperature gradient over the charge was found in a silver crucible with walls 3 mm thick. This crucible, the thermocouples and the charge are presented in Fig. 2.

In the silver crucible were placed two cylinders, the upper of quartz and the lower of silica glass. The cylinders were bored axially to receive the thermocouples. There were two junctions of chromel-alumel, one in the quartz block, thermocouple *A*, and the other in the silica glass block, thermocouple *B*. The E.M.F. of *A* gave the temperature of the quartz block and the E.M.F. across the two chromel leads gave the difference in temperature between the quartz and the glass. As long as no reaction occurred, this differential temperature remained approximately constant, but the heat changes

accompanying the inversion of the quartz caused a sudden acceleration or retardation in the rate of temperature change of the quartz block and hence a "kick" on the reading of the differential couple. The exact method of recording and interpreting the results will be given later.

In the earlier experiments powdered quartz was used. The sample was contained in a divided crucible made of sheet platinum, of the sort described

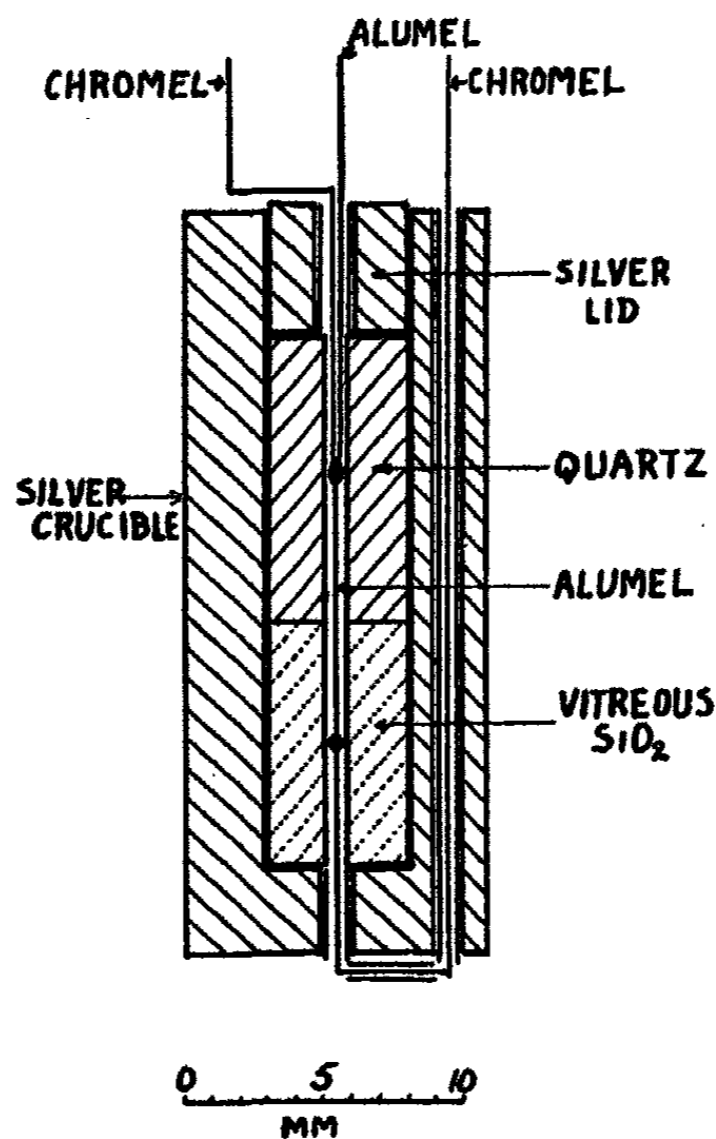


FIG. 2

Silver crucible with charge and thermocouples.

by Smyth and Adams. In one half of the crucible was powdered quartz, in the other was powdered vitreous silica. The method gave results but was not very satisfactory, and indeed was useless between 200 and 700 megabaryes where the temperature gradient was so great that the quartz inverted in layers and heat changes were too diffuse to be detected. The results at high pressures, however, were in good agreement with those obtained when a solid block was used. Between 200 and 700 megabaryes the place of maximum temperature in the furnace rose towards the lid. This, I believe, caused complications in producing changeable E.M.F.'s where the thermocouples ran through the packing and led to a scrapping of the platinum-platinum-rhodium elements which were first employed and to the use of chromel-alumel couples. Disturbances from this source were manifested by a drop in the observed readings between 200 and 700 megabaryes. The evil was never very definitely cured but the results obtained with the chromel-alumel

couple were free from anomalies between 200 and 700 megabaryes and it was assumed that they represented the true temperatures.

Procedure. In an actual experiment a certain pressure was generated in the bomb and the temperature brought to within 50° of the inversion point. The heating current was then cut down until the temperature rose slowly—

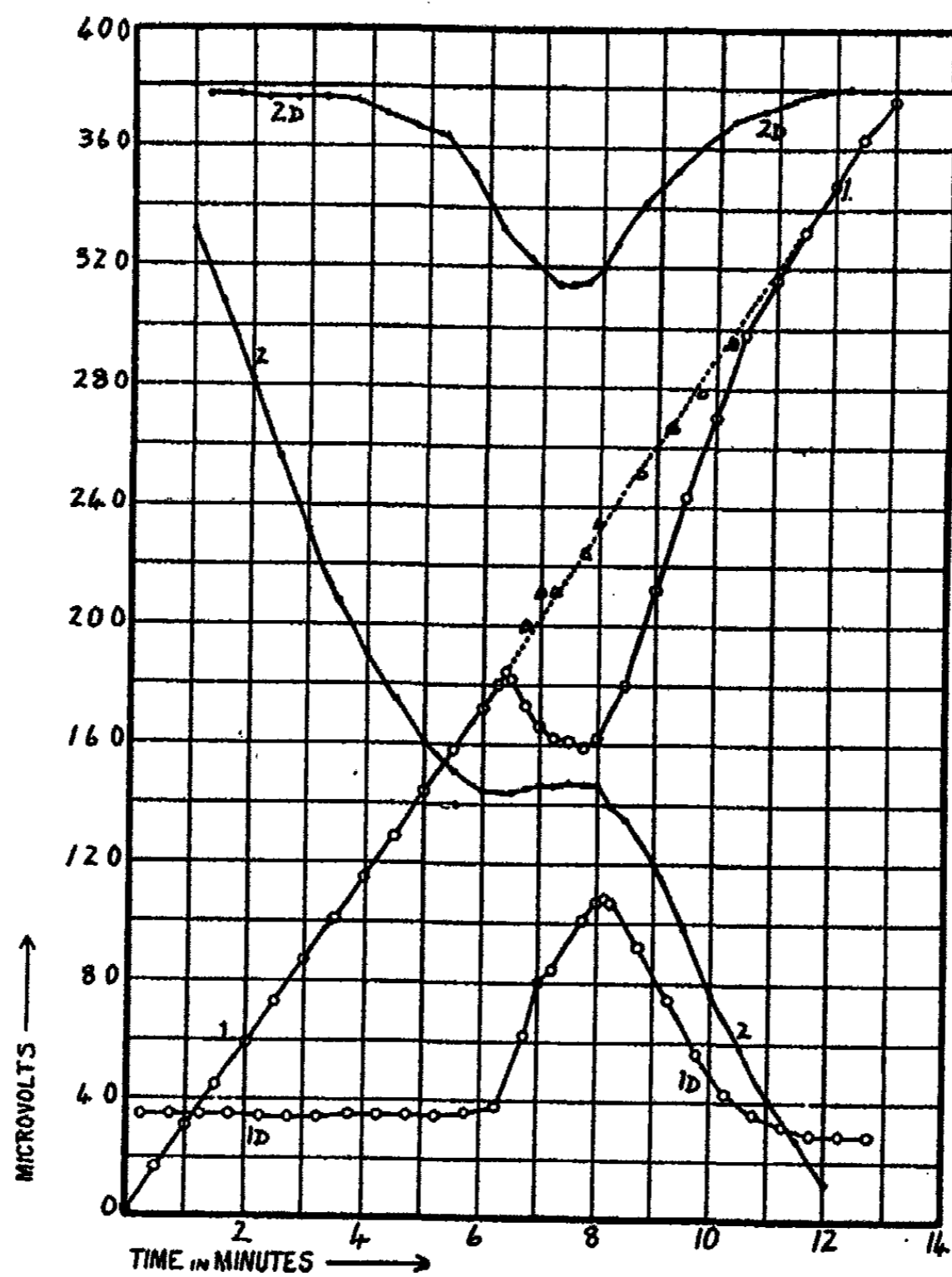


FIG. 3

Typical heating, cooling and differential temperature-time curves.

between 0.3° and 2° per minute. Readings of the temperature of the quartz and of the differential temperature were made every alternate quarter minute. These readings were plotted against time and the usual heating curve was obtained. The point of inversion was taken as the point at which the differential temperature first departed from the normal reading. The justification of this is seen by considering curves 1 and 1D on Fig. 3. Curve 1 is a heating curve for a block of quartz. Curve 1D gives the difference in

temperature between the quartz block and an inert block beside it in the furnace. It will be seen that the differential temperature departs from its normal value at the same time that the break occurs on the heating curve. In the diagram 1D is inverted for the sake of convenience as, of course, the quartz was cooler than the furnace during the inversion.

The chromel and alumel wire from which the thermocouples were made was calibrated at the melting points of zinc and antimony and at the inversion point of quartz at 1 atmosphere pressure. The temperature intervals around 600° were found to agree well with the standard table given in the International Critical Tables, viz., 42.4 microvolts = 1°C.

The results were calculated as follows.

Let T'_0 = the temperature in microvolts of the inversion at 0 megabaryes

T'_p = the temperature in microvolts of the inversion at p megabaryes

Then $T'_p - T'_0 = \Delta T'$, the rise in microvolts of the inversion temperature due to a pressure of p megabaryes. $\Delta T'$ was then converted to ΔT , the rise in inversion temperature in degrees Centigrade, by use of the standard table. In every series of experiments under different pressures a run at atmospheric pressure was made to insure the accuracy of T'_0 .

Results

The results are found in columns 1 and 2 of Table II and are plotted in Fig. 4 with ΔT as ordinate and the pressure in megabaryes as abscissa. The curve is slightly convex towards the pressure axis. A least square quadratic, passed through the points, gave the equation

$$\Delta T = -0.3 + 2.1 \times 10^{-2}p + 8.6 \times 10^{-7}p^2 \quad (1)$$

which corresponds with the curve in Fig. 4.

TABLE II
Observed and Calculated Values of ΔT

| Pressure in megabaryes | ΔT (obs.) °C | ΔT (calc.) °C | obs.-calc. °C |
|------------------------|----------------------|-----------------------|---------------|
| 0 | 0 | -0.3 | +0.3 |
| 130 | 2.4 | 2.5 | -0.1 |
| 220 | 4.6 | 4.4 | +0.2 |
| 340 | 6.4 | 7.0 | -0.6 |
| 540 | 11.4 | 11.3 | +0.1 |
| 750 | 16.2 | 15.9 | +0.3 |
| 940 | 20.8 | 20.2 | +0.6 |
| 1350 | 28.6 | 29.6 | -1.0 |
| 1760 | 39.6 | 39.4 | +0.2 |
| 2210 | 50.9 | 50.3 | +0.6 |
| 2500 | 57.1 | 57.6 | -0.5 |
| 2640 | 61.4 | 61.2 | +0.2 |

It must be emphasized that the E.M.F. of the thermocouples is undoubtedly affected by pressure. An exact knowledge of this effect is lacking but from the influences of pressure on the thermal E.M.F.'s of other metals¹ we may conclude that it is quite small. This conviction was strengthened by a preliminary examination of the effect of pressure on the melting point of antimony. I have, therefore, not corrected the results for the influence of pressure on the thermocouples and in consequence they may at some time be subject to slight modification.

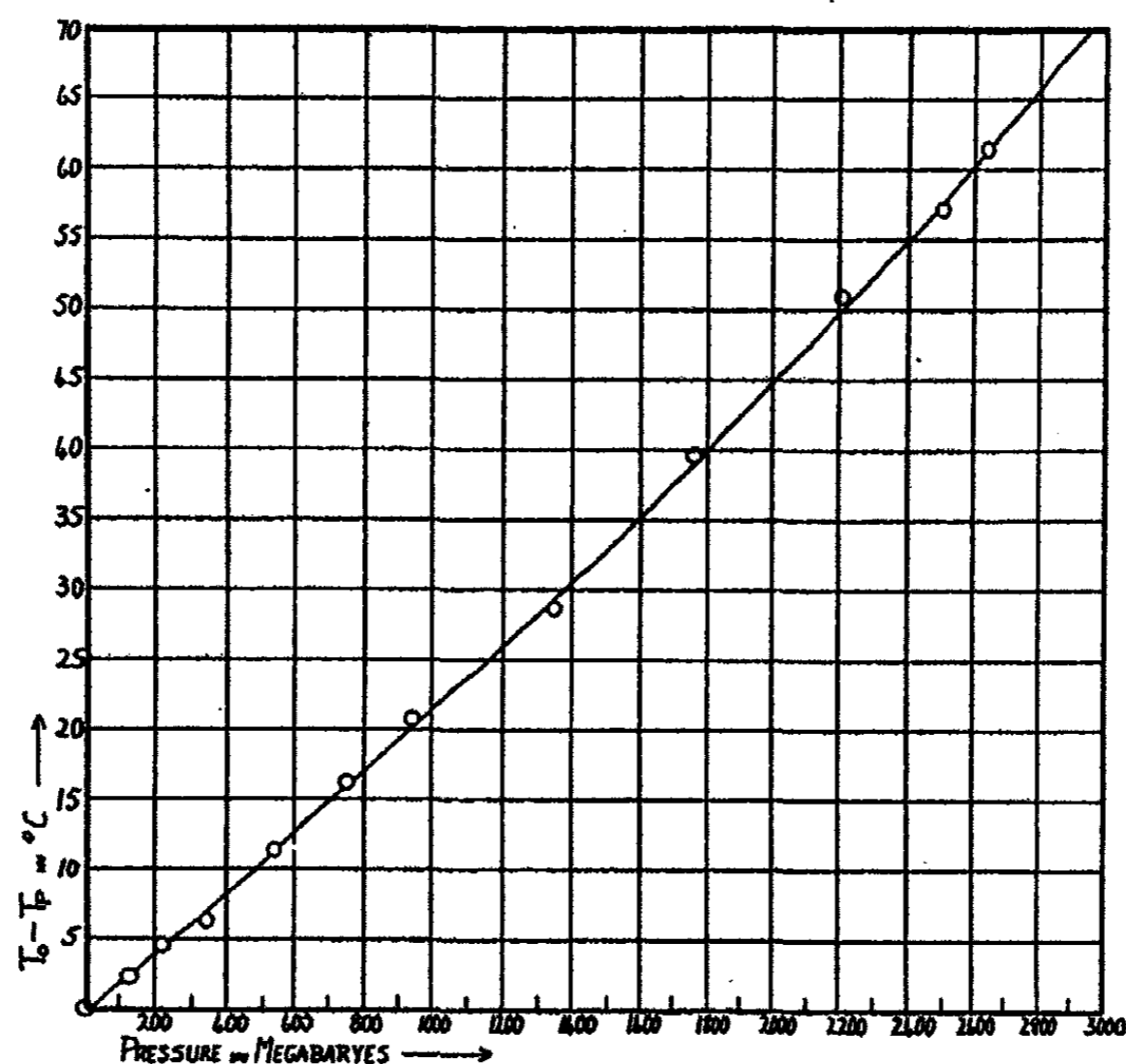


FIG. 4

The rise in inversion temperature corresponding to various pressures

From equation (1) it follows that the initial value for the pressure coefficient of the temperature of the inversion point of quartz, dT/dp , is 2.1° per 100 megabaryes.

In Table III approximate values of the inversion point of quartz at several depths inside the earth are given. The values above 9 km, being extrapolated, must not be assigned a reliability at all comparable with the other values.

Calculation of the Latent Heat of Inversion. From the value of dT/dp at zero pressure, viz. 2.1×10^{-2} degrees per megabarye, and the "instantaneous volume change," it is possible to calculate the latent heat of inversion with the help of the Clausius-Clapeyron equation:

¹P. W. Bridgman: Proc. Am. Acad. Arts Sci., 53, 269 (1918).

$$\frac{dT}{dp} = T \frac{\Delta V}{\Delta H}$$

Now $\frac{dT}{dp} = 2.1 \times 10^{-2}$, $T = 846^\circ\text{K}$, $\Delta V = 3.25$ cc per kg.

$$\therefore \Delta H = \frac{274950}{2.1} \text{ decijoules per kg} = 3.1 \text{ cal. per gram.}$$

The latent heat of the high-low inversion is, therefore, 3.1 cal. per gram. The best experimental values of this latent heat are shown in Table I, column 2. It will be seen that the value just calculated occupies a mean position and is fairly close to 2.5 cal. per gram, which Sosman has given as the most probable estimate of the latent heat of inversion.

TABLE III
The Inversion Temperature of Quartz at Various Depths in the Earth, assuming an average density of 3.0

| Depth in km | Pressure in megabaryes (approx.) | ΔT °C | Temperature of Inversion in °C |
|-------------|----------------------------------|---------------|--------------------------------|
| 0 | 0 | 0 | 573 |
| 1 | 300 | 7 | 580 |
| 5 | 1500 | 33 | 606 |
| 9 | 2700 | 63 | 636 |
| 10 | 3000 | 71 | 644 |
| 20 | 6000 | 157 | (730) |
| 30 | 9000 | 259 | (832) |
| 40 | 12000 | 376 | (949) |
| 50 | 15000 | 509 | (1082) |

Summary

When quartz is subjected to a uniform hydrostatic pressure of p megabaryes, the temperature of its high-low inversion is raised according to the following equation:

$$\Delta T = -0.3 + 2.1 \times 10^{-2} p + 8.6 \times 10^{-7} p^2.$$

This equation expresses the results of direct experimental observations made between 0 and 3000 megabaryes. From the initial pressure coefficient and the instantaneous volume change during the transformation it follows that the latent heat of inversion is 3.1 cal. per gram.

It is a pleasure to acknowledge the advice and criticism with which Dr. L. H. Adams has helped me immensely during this investigation. My thanks are also due to Drs. E. V. Shannon and W. F. Foshag of the U. S. National Museum for furnishing me with the specimens of quartz which I used in this work.

*Geophysical Laboratory,
Carnegie Institution of Washington,
April, 1928.*

A NOTE ON THE HIGH-LOW INVERSION OF QUARTZ AND THE
HEAT CAPACITY OF LOW QUARTZ AT 573°

BY R. E. GIBSON

It has been shown definitely¹ that the high-low inversion of a crystal of quartz is a phase change which is always accompanied by superheating. As the reaction is so rapid that it might be considered as proceeding adiabatically I thought it possible to calculate the heat capacity of low quartz at 573°. This may be done as follows.

Let T_2 = the maximum temperature to which the crystal superheats
 T_1 = the minimum temp. to which it cools during the reaction
 ${}_1H_{T_1}$ = the heat content of the lower phase (low quartz) at T_1
 ${}_1H_{T_2}$ = the heat content of low quartz at T_2
 ${}_2H_{T_1}$ = the heat content of high quartz at T_1
 C_L = the average heat capacity of low quartz between T_1 and T_2
 L = the latent heat of inversion at T_1 ; $L = {}_1H_{T_1} - {}_2H_{T_1}$

Then ${}_1H_{T_1} + C_L(T_2 - T_1) = {}_1H_{T_2}$
 But ${}_1H_{T_2} = {}_2H_{T_2}$ if the process is adiabatic.
 $\therefore {}_1H_{T_1} + C_L(T_2 - T_1) = {}_2H_{T_2}$
 $\therefore L = C_L(T_2 - T_1)$.

If L and $(T_2 - T_1)$ are known we may make an estimate of C_L . In the preceding paper I have calculated a value of the latent heat of inversion from what seems to be the best value of the volume change and the pressure coefficient of the inversion temperature. This gives $L = 3.1$ cal. per gram.

$T_2 - T_1$ has been measured by Bates and Phelps for many different specimens and is given the mean value of 0.5°. In the following I shall outline several experiments made with blocks of quartz in which $T_2 - T_1$ seemed to be nearer 0.9°. Bates and Phelps do not indicate what steps were taken to ensure good contact between the thermocouple and the quartz but their results are consistent and so as an approximation I shall take 0.7 as a tentative value for $T_2 - T_1$.

Hence $C_L = 3.1/0.7 = 4.4$.

The outside limits for C_L , taking the extremes in the values for $T_2 - T_1$, are 3 and 5 cal. per gram per degree.

We have therefore the result that the heat capacity of low quartz in the neighborhood of the high-low inversion is 4 ± 1 . This is more than ten times the heat capacity of low quartz at 550° or of high quartz at 600°. White, and Perrier and Roux,² have shown that the heat capacity of quartz builds up with increasing rapidity above 500° and a very high value of the heat capacity is to be expected. Despite this effect, however, the value just ob-

¹ Bates and Phelps, Bur. Standards Sci. Papers (No. 557) 22, 315 (1927).

² Sosman: "The Properties of Silica," p. 337 (1927).

tained is astonishingly high and it was thought worth while examining the validity of the assumptions underlying the foregoing calculation.

We have assumed in this calculation:

- (1) that the reaction is rapid.
- (2) that the whole block inverted while the temperature dropped from T_2 to T_1 . Assumption number (1), made necessary to avoid confusion with sluggish transformations, is borne out by experiment. All observers agree that the reaction is quite rapid.

The second assumption will be reasonable if it can be shown that T_1 is always above the equilibrium temperature, i.e., the temperature at which the change is thermodynamically reversible.

I hope to demonstrate in this paper that the equilibrium temperature of the 573° inversion of quartz is the maximum temperature reached during the high-low transformation on cooling, and as this is always several tenths of a degree below T_1 , we may say that the above calculation is fairly sound.

Experimental

Heating and cooling curves for blocks of quartz. Two cylinders of quartz were studied. The first, cut from a crystal of vein quartz from Hot Springs, Arkansas (National Museum No. 83660) was 19 mm long and 12 mm in diameter. The second was cut from a pebble of quartz from Brazil and was 19 mm long and 10 mm in diameter. Both were drilled axially to a depth of 11 mm and in these holes thermocouples were placed. It should be emphasized that the thermocouple fitted tightly in the hole so that good contact was made between the element and the quartz.

The blocks were enclosed in thick-walled silver crucibles, placed in a platinum furnace and heating and cooling curves were made in the usual way, temperature readings being taken every quarter of a minute. Chromel-alumel couples were used. The sensitivity of these is quite high, 42.4 microvolts being equivalent to 1°C . The couples were calibrated at the freezing point of antimony (630°).

A series of orienting experiments confirmed Bates and Phelps' observations as to the superheating and supercooling phenomena. Curves 1 and 2, Fig. 1, show the results. It will be seen that the drop in temperature during the low \rightarrow high transformation is as great as 1°C but that the rise of temperature during the high \rightarrow low change never exceeds 0.2° . The comparative flatness of the maxima on the cooling curves, taken in conjunction with the small supercooling, led to the thought that the equilibrium temperature was close to the highest temperature reached after supercooling.

To test this hypothesis I tried to reverse the reaction during the high \rightarrow low inversion. The temperature of the furnace was allowed to fall slowly until the minimum on the heating curve indicated the change was taking place. Thereafter, at a convenient time, the current through the furnace was doubled. The cooling stopped almost instantly and the block started to gain heat from the furnace. The results are given in curves 3, 4 and 5

(Fig. 1). The arrows indicate when the reheating was started. In cases 3 and 4 the heating was begun before the maximum temperature was reached. The temperature of the block remained practically constant for a fraction of a minute and then rose steadily and rapidly. In case 5, however, where reheating was not begun until after the maximum on the cooling curve had been passed, the curve exhibited no preliminary flattening, the temperature rose immediately, the low quartz superheated and then inverted with the usual drop in temperature. About twenty experiments in all were made. The results were all entirely similar to those given in the figures.

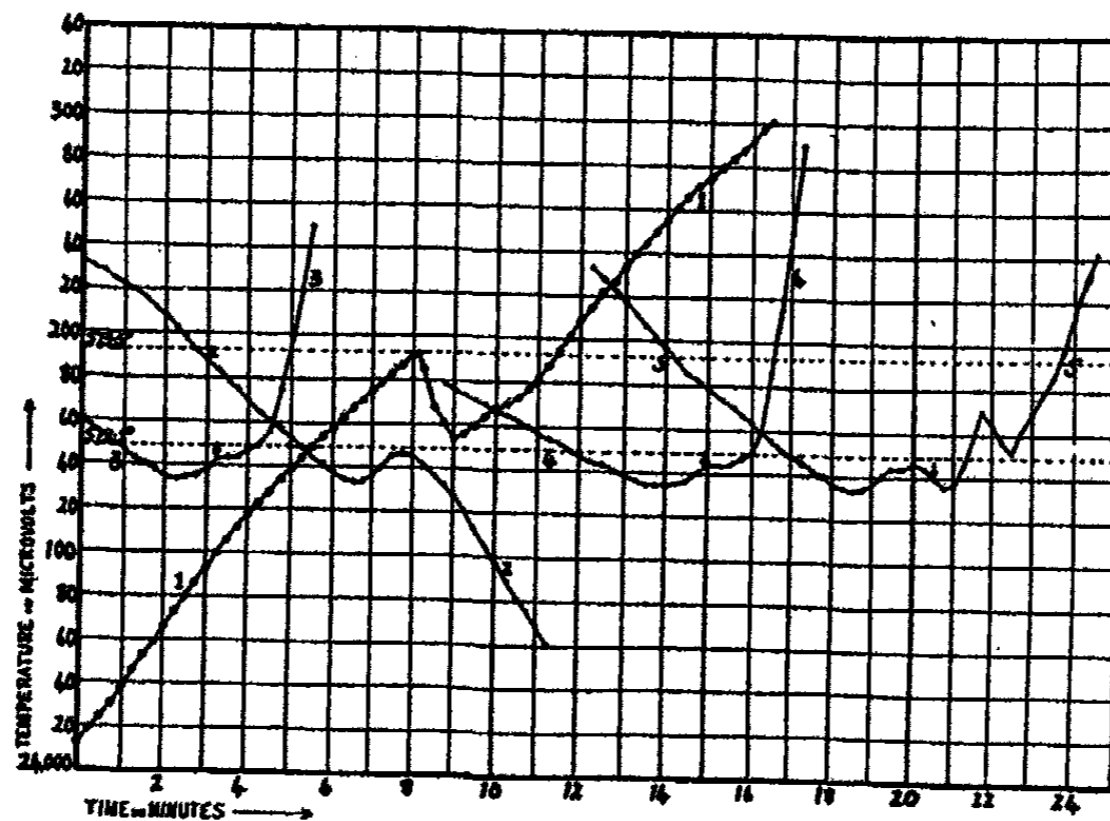


FIG. 1
Heating and cooling curves for a block of quartz, illustrating reversal of the high \rightarrow low inversion.

It would seem, therefore, that, if reheating of a quartz block is begun at the maximum on the cooling curve or just before it, the low quartz present is converted to the high variety without appreciable superheating. If, however, the maximum is passed, indicating that the high-low inversion has gone to completion, then, on reheating, the low-high change is accompanied by superheating. The parallelism between this phenomenon and the presence or absence of the solid phase during the freezing of a liquid which supercools readily is too obvious to require emphasis.

One is perhaps justified in saying that about the temperature of this maximum ($572.3 \pm 0.2^\circ$) low and high quartz coexist in equilibrium or at any rate behave thermodynamically as if they did. We may also conclude that the difference in the observed temperature of the up and down inversions is solely a matter of superheating and supercooling, and is not due to a real difference in the temperatures of these two changes.¹

¹ For other explanations see Sosman: *op. cit.*, p. 122.

It should be emphasized that these experiments refer to a sound, solid block of quartz. The effect of shattering on a block is shown in Fig. 2. Curves 1 and 1' were made with a sound block; curves 2, 3, 2' and 3' with exactly the same block half an hour later when it had been shattered by bringing it extremely rapidly through the inversion.

The chief features of interest are the lessening of the temperature drop during the low \rightarrow high inversion and the flattening of the cooling curve. I

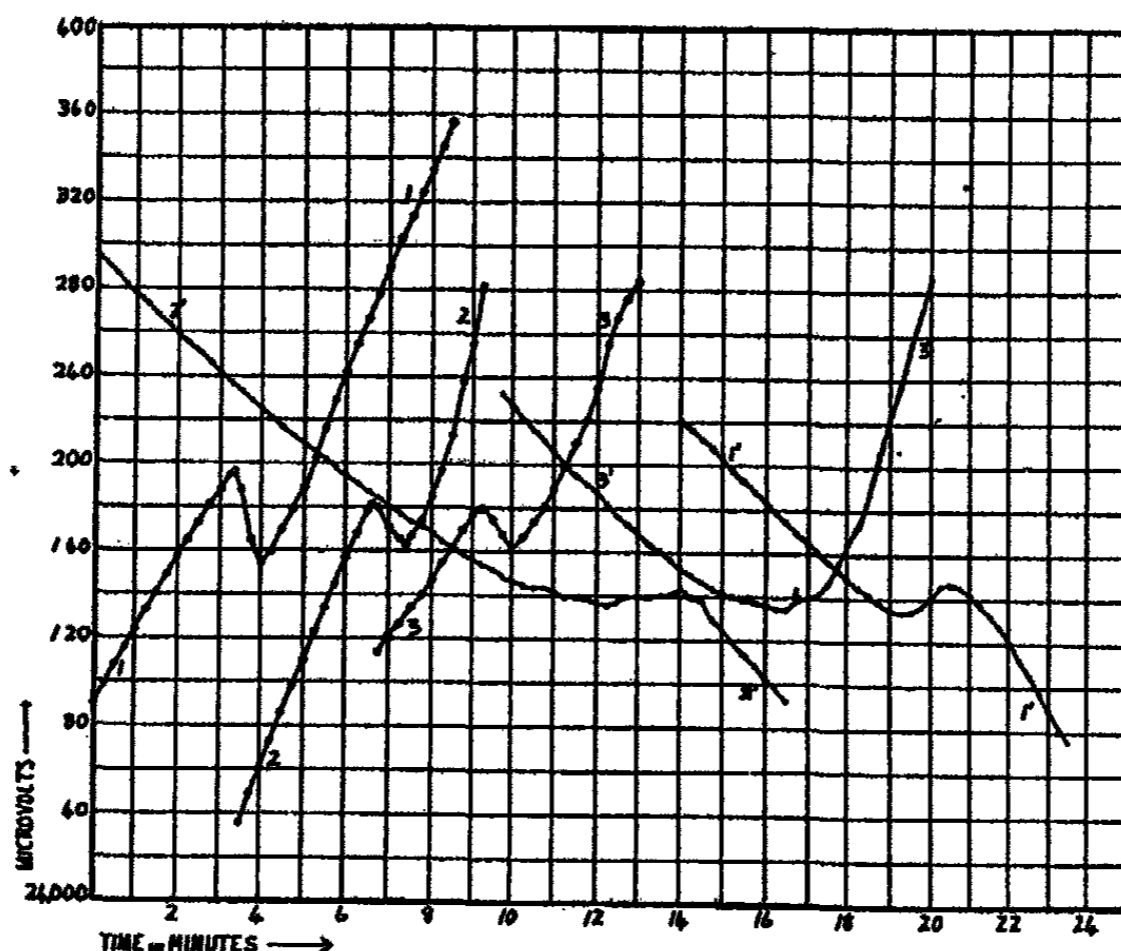


FIG. 2
Heating and cooling curves for a broken block of quartz.

attribute these differences to the individual fragments' inverting at different times. The heat changes are thus distributed in time and the effect on the thermocouple is thereby diminished.

In one series of experiments with a broken block of Arkansas quartz the cooling curves were almost parallel to the time axis during inversion. There was practically no supercooling. An example of this is seen in curve 2, Fig. 3, of the previous paper.

There is a difference of 0.3° in the maxima on the heating curves before and after breaking but the maximum on the cooling curve is altered by only 0.05° . Curve 3' gives another illustration of the reversal of the reaction during the high \rightarrow low change. I have included the curves for a cracked block because they demonstrate that the constancy of the temperature of the maximum on the heating curve (573.3°) for a solid block is perhaps a matter of accident and that the fundamental temperature of this reaction is $572.3 (\pm 0.2)$, the equilibrium temperature of the reaction.

Conclusion and Summary

The high-low inversion of a crystal of quartz at one atmosphere pressure is a change of phase which is generally accompanied by superheating and supercooling. There seems, however, to be a temperature (572.3 ± 0.2) at which low quartz may be converted reversibly to high quartz and were it not for almost insuperable experimental difficulties it would be possible to have the two phases in equilibrium at this temperature. This renders unnecessary any hypothesis of forced inversion.

Before a block of low-quartz passes to the high variety it superheats so much that during the inversion its temperature never falls to the equilibrium value. Therefore, since the reaction is adiabatic, we may calculate the apparent heat capacity of low quartz around 573° . This is 4 ± 1 cal. per gram per degree.

On the changes in physical properties of quartz between 0° and 570° we can throw no light. Quartz at 570° is certainly very different from quartz at atmospheric temperature but quartz at 570° is a definite and stable substance and the inversion at 572.3° , except for the superheating or supercooling, is quite comparable with any rapid enantiotropic change.

*Geophysical Laboratory,
Carnegie Institution of Washington,
April, 1928.*

THE VARIATION OF THE CAPILLARY ACTION OF SOLUTIONS WITH TIME*

BY H. M. TRIMBLE

In a recent paper Washburn and Bigelow¹ have shown that the surface tensions of certain aqueous solutions, as measured by the capillary rise method, vary with time. Using solutes which are more volatile than water, they found a marked increase in this property. Their explanation of the phenomenon is essentially as follows: The height to which a liquid rises in a given capillary tube is determined largely by the cohesive forces which the molecules in the supporting meniscus exert; that is, by the surface tension of the liquid. For a mixture of two liquids the effective surface tension is undoubtedly a function of the composition of the surface; a composite of the cohesive forces of its components. If the solute is, as in the cases which they investigated, more volatile than the water in which it is dissolved, it will escape to the air of the room at a more rapid rate than will the water. This loss of solute can be replaced only in part by diffusion from the main body of the solution, since diffusion in the liquid state proceeds relatively slowly. As a result of this preferential escape of the solute, the composition of the surface changes, and with it the surface tension and the height to which the liquid rises in the capillary. Since the volatile solutes which they used act to lower the surface tension of water, the process should result in an increase in capillary height; as, indeed, it did. The interest and the possible importance of this phenomenon led the author to study it as it is manifested by various mixtures of organic substances.

Apparatus

The capillarimeters which were used were of the three types shown diagrammatically in Fig. 1. Of these, types A and B have been described by Washburn and Bigelow. (Loc. cit.) Type C was constructed to provide for the sweeping away of the vapors by means of a stream of air, as they issued from the capillary tube; thus, in effect, eliminating the portion of tubing which was above the capillary tube in the other two forms. Its nature will be clear from the diagram.

All tubing through which measurements upon the positions of menisci were to be made was chosen so as to be uniform in diameter, and free from striations or other optical defects. Measurements were made upon a selected portion of a millimeter scale placed within the larger tubes, and upon threads of mercury in the capillary tubes; and those tubes were chosen for which these measurements, in different positions, were constant to within ± 0.02 millimeters. A comparator of standard make was used in this work. It was found later that the possible error introduced in the variation above men-

* Contribution from the Chemistry Laboratory of the University of Michigan.

¹ E. R. Washburn and S. L. Bigelow: *J. Phys. Chem.*, 32, 321-53 (1928).

tioned was well within the limits of accuracy of the experiments as a whole. The mercury threads used in examining the capillary tubes were then expelled and weighed and the average radii of the tubes were calculated. With soft glass capillaries there was no great difficulty in finding portions as long as one to three centimeters which were satisfactorily uniform. Such portions were marked by rings etched in the glass and used in subsequent experiments. Two pieces of Pyrex capillary tubing were found, each about five centimeters in length, which were very uniform throughout. They were used in the major portion of the work which is here discussed.

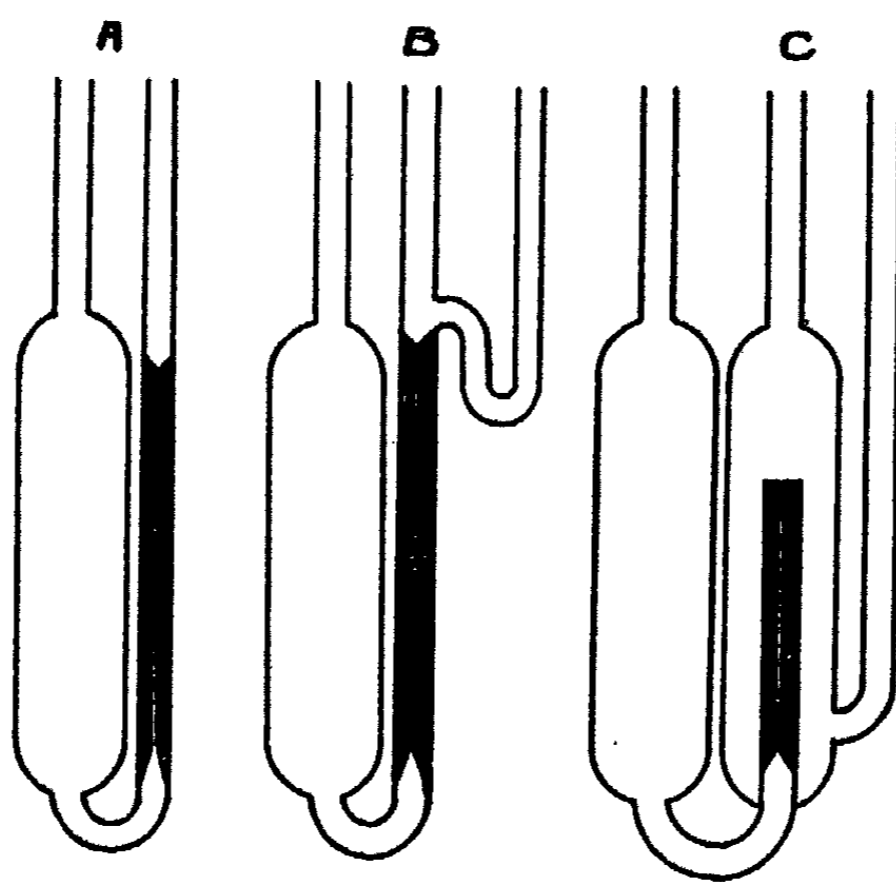


FIG. 1
Capillarimeters.

Since it was desirable to avoid the necessity of correcting the height of the meniscus for the capillary rise in its tube, small tubing could not be used in the larger arm of the capillarimeter. Calculation by the method of Lord Rayleigh¹ shows that, for a liquid whose specific cohesion, a^2 , is 7, in a tube of radius 14 millimeters, the correction involved is less than 0.02 millimeters. Since no liquid or mixture of higher capillary constant than about 7 was to be used, the large arms of the capillarimeters were made of tubing of this size. After being built into capillarimeters, the capillary tubes were further tested for constancy of internal diameter by determining the heights to which carefully purified benzene rose in them at various places in the uniform portions at 20°C. They were found to be uniform within the limits previously set, and the diameters as calculated from the capillary rise agreed very well with those previously determined.

¹ Lord Rayleigh: Proc. Roy. Soc., 92A, 184 (1915).

All experiments were carried out in thermostats provided with plate glass windows. That portion of the front window through which the positions of menisci were to be read was tested and found to be very uniform.

The large meniscus was illuminated by the method of Richards and Coombs.¹ Readings were made by means of two cathetometers provided with low power microscopes mounted upon micrometer slides. By means of these instruments it was possible to read directly to 0.01 and 0.005 millimeters, respectively. Care was taken to have both the large and the small meniscus clearly in focus at the time of making a measurement.

Materials

All the organic substances used were the best standard "C.P." commercial products. Each liquid, with one exception, was dried over a suitable dehydrating agent and fractionated just before using, rejecting large first and last portions. Pentane, which had been prepared from petroleum in the laboratories of the Eastman Kodak Company, was not further purified.

The Experiments

Cleaning of Capillarimeters. All capillarimeters were cleaned by washing them out with alcohol; allowing them to stand over night or longer filled with freshly prepared aqua regia; and then, finally, washing them thoroughly with boiling conductivity water. The liquids were always drawn out of a capillarimeter through the capillary arm with the aid of a filter pump. After washing, the capillarimeter was dried in a hot air bath, drawing filtered air through it repeatedly during the process. After this treatment the apparatus was almost invariably found to be satisfactorily clean.

Experimental Procedure. Mixtures of organic liquids for the experiments were made up by weight as wanted. Since the composition of a mixture of volatile substances may be slightly changed in pouring from one vessel to another, the flasks in which the solutions for study were prepared were converted into "wash bottles" by inserting rubber stoppers provided with pressure and delivery tubes; and this device was used in transferring the liquids. Such an amount was introduced into a capillarimeter as would bring the meniscus in the capillary tube to some desired position within its uniform portion. The capillarimeter was then put into the thermostat in the proper position and left for twenty to thirty minutes to take the temperature of the bath. The experiment was then started. The liquid was drawn out of the capillary tube by applying suction through a rubber tube attached to the outlet tube of the larger arm, and thoroughly mixed by successive blowing and drawing. During this process, which was continued for one or two minutes, the walls of the capillary were well cleared of liquid by drainage and by evaporation. When the mixture was allowed to run up the tube again, no droplets formed above it if it was satisfactorily clean. Such droplets must be avoided if the experiment is to be successful.

¹ Richards and Coombs: J. Am. Chem. Soc., 37, 1656-76 (1915).

The cathetometer had previously been brought into position and leveled. Its cross-hair was now brought to the approximate position of the small meniscus at its equilibrium height. The agitation was then repeated as above described, the meniscus was allowed to run up the tube about thirty seconds before the time set for beginning the experiment, and the cross-hair of the microscope was quickly brought to exact tangency with the lower edge of its image. The meniscus was then made to oscillate about its initial position by alternately applying the finger to the opening of the capillary arm and removing it, until the second hand of a watch used in timing the experiment was just passing its zero position, when the agitation was stopped. The changes, if any occurred, always started immediately, and the readings were taken at suitable intervals thereafter.

It was found that in successive experiments, carried out as above described, and starting again with the same mixture, the results were reproducible to within about one percent. Much more consistent results were gotten, however, if the experiment was repeated with a fresh mixture after recleaning the capillarimeter. This was done in the great majority of cases. All experiments were carried out at 25° C unless otherwise stated.

Effects of Tube Length, and of Tube Size. If the preferential evaporation theory be accepted as a satisfactory explanation of the phenomenon under consideration; then the rate of diffusion of the vapors away from the capillary meniscus will determine the rate at which the surface energy of the solution changes. Other things being equal, it would seem that this diffusion and the corresponding rise of liquid in the capillary tube, should be more rapid the shorter the tube above the meniscus, and the greater its cross sectional area. This matter was the first to be investigated.

For reasons which will be explained below, it was found to be impossible, in general, to express the results of experiments in the usual terms, that is, in terms of dynes per centimeter, or in terms of the capillary constant, a^2 . Instead, the height of the meniscus in the capillary above that in the large tube as it was found in the experiments has been used in almost every case. This height is called the "capillary rise" in the discussion which follows.

In a few preliminary experiments it was found that mixtures of ethyl ether with benzene, with toluene, and with acetone all showed consistent increases in capillary rise with time. Studies of the effect of tube length were carried out with all of them in capillarimeters of type A. The experiments at 25°C with an ether-toluene mixture in which the mol fraction of each was 0.5 were typical. The results, in terms of capillary rise in a tube of radius 0.214 mm. for various tube lengths, are shown in Fig. 2. Each curve represents the mean of the data found in at least two,—generally more, experiments, whose results agreed to within 0.25%. Tube lengths were measured from the bottom of the capillary meniscus to the top of the capillary tube. In each case the wide tube above the capillary had its influence upon the phenomenon, of course, but this was not taken into account at this time. As will be seen, the rate of rise of liquid in the tube increases with decrease in tube length. Experiments in capillary tubes of radii 0.167 and 0.246 mm., and

with mixtures of ether with benzene and of ether with toluene, at various concentrations, gave, qualitatively, the same result.

The effect of tube size was next studied. Capillarmeters of type A were prepared, using small tubes of radii 2.54, 1.05, 0.77, 0.43, 0.35, 0.246 and 0.167 mm., respectively. The results with an ether-acetone mixture, in which the ether was present at a concentration of 0.412, in terms of mol fraction, are shown in the curves of Fig. 3. The capillary meniscus was, in these

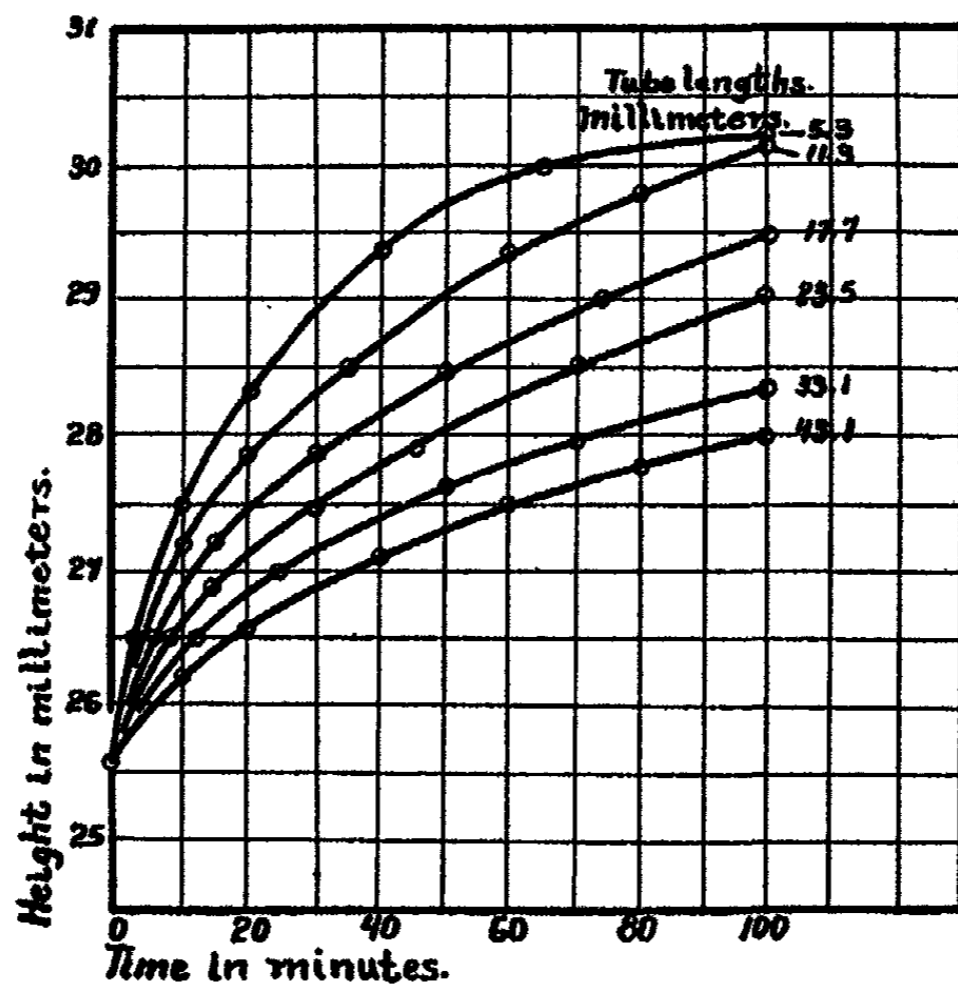


FIG. 2
Effect of tube length.

experiments, started at a point 5 mm. below the upper end of the capillary tube. Rates of rise as found with the various capillarmeters could not give comparable curves, since the tube sizes were different; and so the capillary rises at the start, as well as the rates of rise due to changes in the surface forces, would be quite different for different tubes. In this case hr , the product of the capillary rise by the radius of the tube, has been plotted against time. This product is employed here simply for convenience in representing the data, and must not be confused with a^2 , the specific cohesion of the mixture of liquids. It cannot be taken as characteristic, in general, of the capillary activity of any mixture which is evaporating, as will be explained below. It is noteworthy that the tube of radius 2.54 mm. failed to show an appreciable rise at all. Results very similar to these were found with mixtures of ether and toluene and of ether and benzene. Other tube lengths were also tried with all these liquids, with much the same results.

In the sets of curves of Figs. 2 and 3, it will be observed that the uppermost ones are abnormal in form. In these experiments it was observed that at the time when the abnormality appeared, the liquid had risen to the top of the uniform capillary tube, and was spreading into the larger tube above.

Effect of Densities, Volatilities, and Surface Tensions of the Components. A study of the change of capillary height with time was next carried out with mixtures of pairs of organic liquids, chosen so as to give rather wide variations in density, volatility and surface tension; other factors, which it seemed, should greatly influence the nature and extent of the phenomenon. Capil-

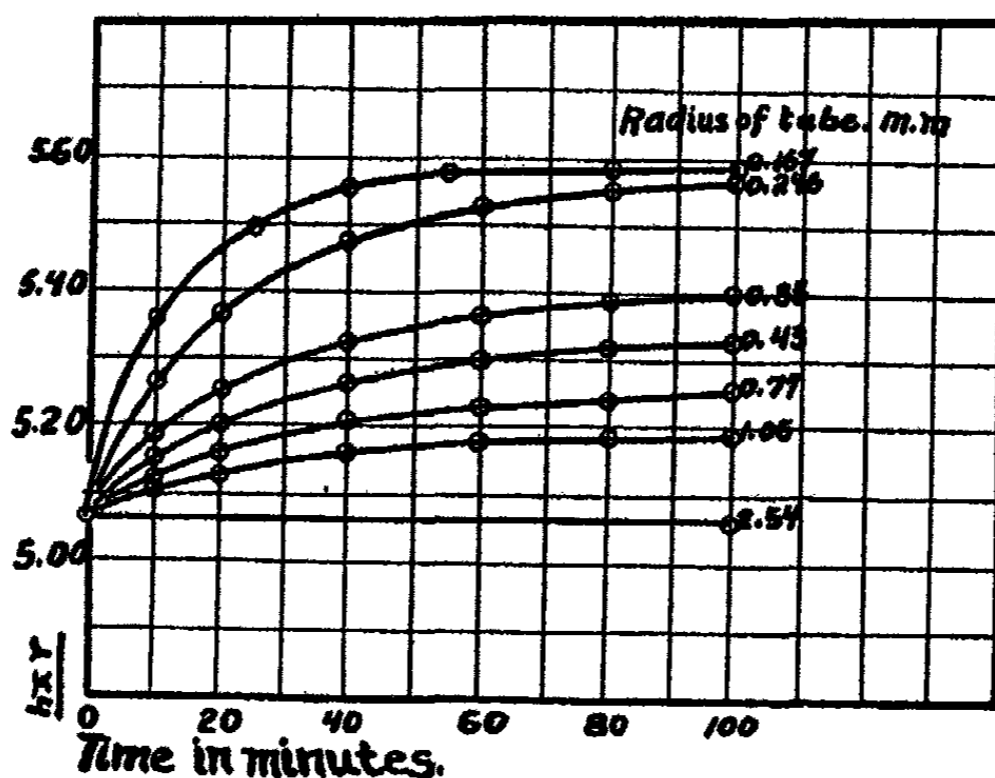


FIG. 3
Effect of tube size.

larimeters of type A, of nearly the same dimensions, were employed. The capillary tube in one of them had an average radius of 0.213 mm. and that in the other had a radius of 0.216 mm. The capillary meniscus was, in every case, started 10 mm. below the top of the capillary tube. The changes found in a few typical cases are shown in Fig. 4. These curves are all drawn to scale, and so they show the relative magnitudes of the changes in the various cases as found.

The nature of these changes will be discussed and, at the same time, explained with the aid of Table I, in the light of the theory of preferential evaporation given above. Columns 2, 3, 4 and 5 of the table give, respectively, the vapor pressures, densities, surface tensions, and capillary rises of the pure liquids named in a tube of radius 0.214 mm. at 25°C.

When a mixture of ether and toluene is allowed to evaporate in one of these capillarimeters, the ether escapes preferentially from the capillary meniscus because of its greater volatility. Its escape results in an increase of surface energy accompanied by a rise, since thereby the surface is enriched in toluene, which has the higher surface tension. This change is shown in

TABLE I

| | P mm. Hg. | d_{40}° | γ | h |
|-------------------------------------------------|-----------|------------------|----------|------|
| CS ₂ | 361 | 1.2559 | 31.5 | 23.9 |
| C ₆ H ₅ CH ₃ | 27 | 0.8591 | 28.0 | 31.0 |
| (C ₂ H ₅) ₂ O | 526 | 0.7099 | 16.7 | 22.4 |
| CH ₃ COCH ₃ | 226 | 0.7863 | 22.8 | 27.7 |
| CCl ₄ | 114 | 1.4835 | 26.3 | 15.8 |

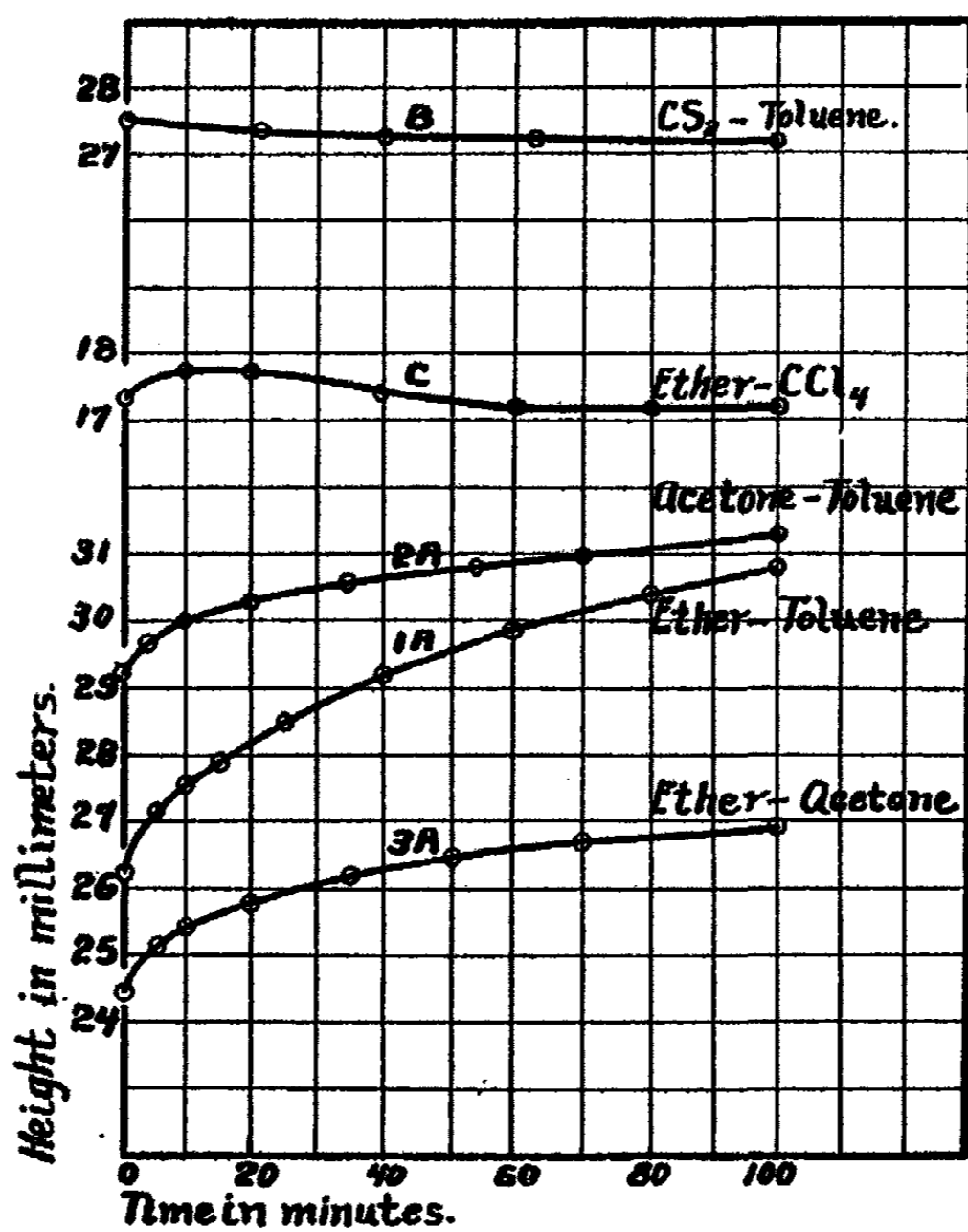


FIG. 4
Changes with various pairs.

curve 1 of type A. The effects with two other such pairs are shown in curves 2 and 3. The differences in vapor pressure and in surface tension of the components of these mixtures are less than in the first case, and the capillary rises are correspondingly less rapid and less extensive.

Again, carbon disulfide has a greater vapor pressure than has toluene; and so escapes preferentially from the surface of a mixture of the two. This removes the substance of greater surface tension, and so the height of the column falls. This change is shown in curve B. It will be noted that the rate

of fall is surprisingly low, considering the differences in vapor pressure and surface tension between these two substances.

Curve C illustrates another kind of behavior, where the capillary height first increases, comes to a maximum, and then decreases.

A fourth type of change, in which a fall to a minimum would be succeeded by a rise might be expected. It has not been found in the course of these experiments.

Mixtures of benzene with toluene and of carbon tetrachloride with chloroform showed no change whatever in these experiments, probably because the liquids of these pairs are very similar in their properties.

Most of the mixtures studied gave a change of capillary height, with time, of type A. The pairs ether-carbon disulfide, ether-nitrobenzene, and ether-amyl alcohol, gave much more pronounced increases in capillary height than any of those whose behavior is shown in Fig. 4. In each of these cases ether, with high volatility and low surface tension, is paired with a substance of low volatility and comparatively high surface tension. Pentane, which is much like ether in density, volatility and surface tension gave changes nearly as pronounced as did ether in mixtures with toluene, carbon disulfide and acetone. Every mixture whose more volatile component had also a lower surface tension than the other substance in the mixture showed a change of this kind, provided that the two did not differ greatly in density. In no case was a rise greater than 5 mm. found in the course of 100 minutes. All these curves displayed a decreasing slope as time went on; but a condition of equilibrium was reached only after a very long time, if ever, as the capillary height was found still to be increasing slowly in a number of cases, with different pairs of liquids, even after the expiration of 50 hours.

Mixtures of carbon disulfide with benzene, chloroform, and carbon tetrachloride also showed a decrease in capillary height, with time, of the same kind as is shown in curve B of Fig. 4.

Mixtures of pentane and of acetone with carbon tetrachloride; and of ether with chloroform showed the same rise to a maximum, succeeded by a fall as that shown in curve C of Fig. 4.

Mixtures of the various pairs of liquids named above in other proportions were also used. The tube sizes, the tube lengths and the temperatures were varied somewhat in different experiments. The results found differed from those which have been given in degree in every case, but never in kind.

These results are, with the exception of curves of type C, just what anyone with the data before him might have anticipated. In experiments with many binary mixtures formed from some 25 organic liquids, predictions of changes in capillary height from the vapor pressures and surface tensions of the components were amply verified in a qualitative way in nearly all cases.

The effect of the difference in density between the components of a given mixture upon the phenomenon was the cause of much uncertainty in any attempts at quantitative prediction. This effect is most apparent in the case of the mixture of ether and carbon tetrachloride whose behavior is shown in

curve C of Fig. 4. Here the capillary height at first increases, due to preferential escape of ether from the surface. After a time, however, the increase in weight of the solution, due to loss of this specifically lighter component, first balances the increase in surface energy and then exceeds it in its effect; and the curve passes through a maximum and then falls. Similarly, the escape of the specifically heavier carbon disulfide from its solution in toluene, the mixture whose behavior is shown in curve B makes the mixture progressively lighter, and so undoubtedly acts to retard the rate of fall of the meniscus. Mixtures of ether with any of the other substances named must become specifically heavier as the ether evaporates, and this change undoubtedly acts to decrease the rate of rise of the liquid in the capillary. Thus, the effect of differences in density between the components upon the nature of the phenomenon under consideration is never negligible, and it may be of prime importance in the behavior of some mixtures.

Convection Currents in Capillary Tubes. It was believed, in the earlier part of this work, that the process by which the components of a mixture reach its surface involves only simple diffusion, unaided by any kind of mechanical stirring. If this were the case, then the alteration of the density of the solution with time could be described in terms of some such generalization as Fick's Law of diffusion, and the data might yet prove susceptible to mathematical treatment so as to make possible quantitative predictions. But one afternoon it was found, while working with a mixture of ether and acetone, that a tiny mote of some foreign substance had gotten into the liquid just below the capillary meniscus. There it remained, moving around and around in a path such as is shown in Fig. 5. This behavior was quite unexpected, so it was followed with great interest, and in detail. The time required for it to traverse this path was about one second. The rise in the capillary tube went on in this experiment in quite the usual manner, giving a normal curve. The meniscus was twice drawn down to reform the surface, and each time the usual rise took place; the particle meanwhile keeping up its regular motion. It was still present and actively in motion when the experiment was terminated after eighteen hours.

The occurrence of such a mote in a mixture is, of course, quite accidental. It happened in two other cases, however; once with a mixture of ether and toluene and once with a mixture of carbon disulfide and ether. In both cases the mote behaved in the same manner as did the one first studied.

These motes served to show, by their motion, the motion of the liquid in which they were suspended. It seems clear that specifically heavier liquid was flowing down the outer portion of the liquid mass from the region where the meniscus made contact with the walls of the tube, and where the most active evaporation was in progress. At the same time, liquid which was specifically lighter was flowing up the middle of the tube to the meniscus

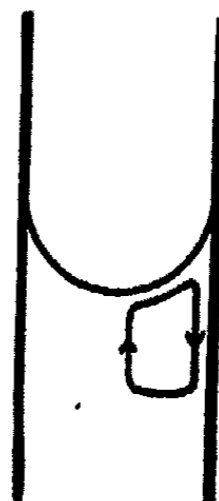


FIG. 5
Convection currents in capillary

and along it to the zone of evaporation at the edges. The amplitude of the motion of the notes in the vertical sense was never greater than about twice the radius of the capillary tube, but the convection currents which it indicated may well have extended much farther down into the solution.

The tube in which these convection currents were first made manifest was 0.214 mm. in radius. The other tubes were only slightly larger. It would be interesting, if feasible, to extend these studies to much larger capillaries. It seems probable to the author, however, that the only difference between the phenomenon as between small and large tubes would be that in the latter the convection currents would be more complex, and the liquid would be actively stirred to much greater depths. This stirring tends to maintain uniformity of composition in the liquid, probably to a greater extent the larger the tube. It seems, then, that we have here the explanation of the fact that the rate of change of capillary height with time falls off rapidly with increasing size of tube. It was found, in the experiments described above, that in a tube of radius 2.54 mm. there was no appreciable change in the height of the meniscus in 100 minutes. In a tube of this size, then, we have reached the condition where convection currents will reduce the rate at which the substance of higher surface tension is concentrated in the supporting surface to almost zero. The abnormality of the uppermost curves of Figs. 2 and 3 may be explained similarly. This mixing by convection currents also explains why changes such as are shown in curves B and C of Fig. 4, where one would be led to expect extensive effects, are, in reality, very limited.

Most important of all, however, so far as expressing the results goes, these experiments show that the composition, and so also the density of a solution which is evaporating in a narrow capillary tube changes in an unknown manner and to a depth which cannot be accurately determined. Evidently, too, the composition of the escaping vapors also varies in an unknown manner. The surface tension of such a solution, then, cannot be calculated by means of the usual formula,¹ $\gamma = \frac{1}{2} rh dg$. Neither can results be expressed in terms of specific cohesion. The product $r h$ cannot be "specific" for the solution. In the first place, its composition varies from moment to moment. Then, too, as has been seen, solutions at the same stage in their evaporation do not give at all the same values of " $h r$ " in capillary tubes of different sizes. For these reasons results have been expressed in terms of "capillary rise" almost entirely in this paper.

Amount of Liquid lost in Experiments. The amount of liquid lost by evaporation in any of these experiments is certainly very small. This was proved by measuring the actual rate at which the meniscus fell in a capillary tube closed at the bottom and filled with liquid. The vapor was allowed to escape freely to the air of the room. In experiments at 25°C, less than 0.04 grams of pure ether was lost from a tube of radius 0.73 millimeters in the

¹ It should be remarked at this point that the densities of the solutes in the mixtures investigated by Washburn and Bigelow, in which preferential evaporation was believed to be responsible for the changes which they found were but little different from that of water.

course of six hours. Mixtures of ether with toluene and with carbon tetrachloride showed a much less rapid escape of vapor from the same tube. The meniscus at the start was two centimeters below the top of the tube in every case.

Effect of Closing Tubes. If a U tube with a ground glass stopper is sealed on in such a manner that it connects the two arms of the capillarimeter, so

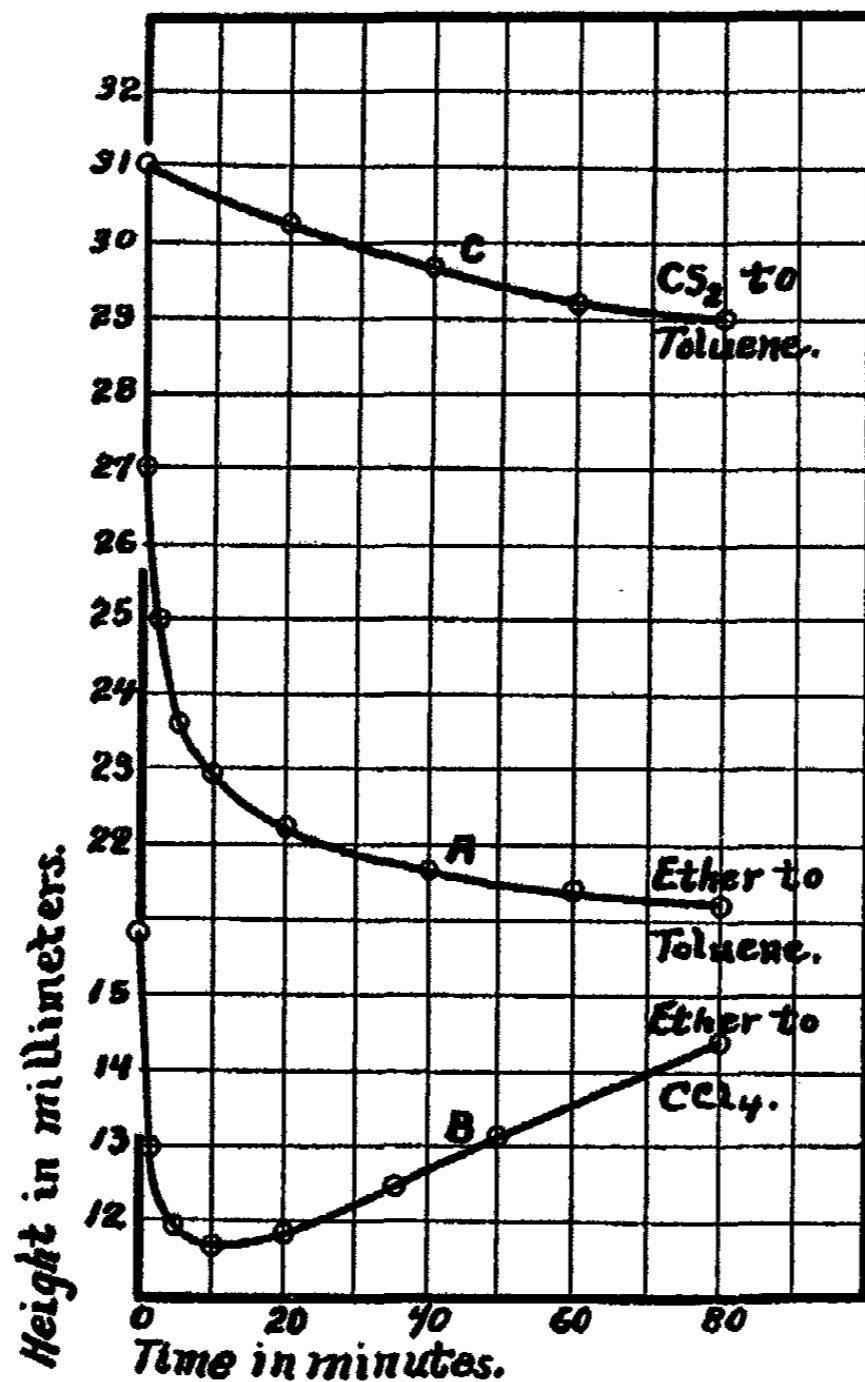


FIG. 6
Volatile substance distilling to liquid.

that the system is completely closed, changes in capillary height with time can be prevented. Rubber tubing cannot be employed, as it is useless in preventing the escape of organic vapors. If a tube is closed after some change in capillary height has taken place, the meniscus slowly returns to its original position. If the tubes are closed from the time of agitation no change ever takes place. This repetition of certain experiments by Washburn and Bigelow confirms further the correctness of their finding; namely, that the phenomenon under consideration is due to the effects of preferential evaporation.

Effect of Evaporation from a Side Tube to the Surface of Pure Liquid. Washburn and Bigelow found that when a capillarimeter of type B is used, pure water being placed in the capillarimeter and the volatile solute in the U tube side arm, the volatile liquid distils to the capillary meniscus and the meniscus falls. This experiment has been repeated with organic liquids; and it has been found possible to duplicate their results, with modifications such as would be expected for these substances. Thus, ether and various other liquids distilling from the side tube to the surface of certain substances of higher surface tension causes the meniscus in the capillary tube to fall. This behavior is shown in curve A of Fig. 6. Ether, when it distils from the

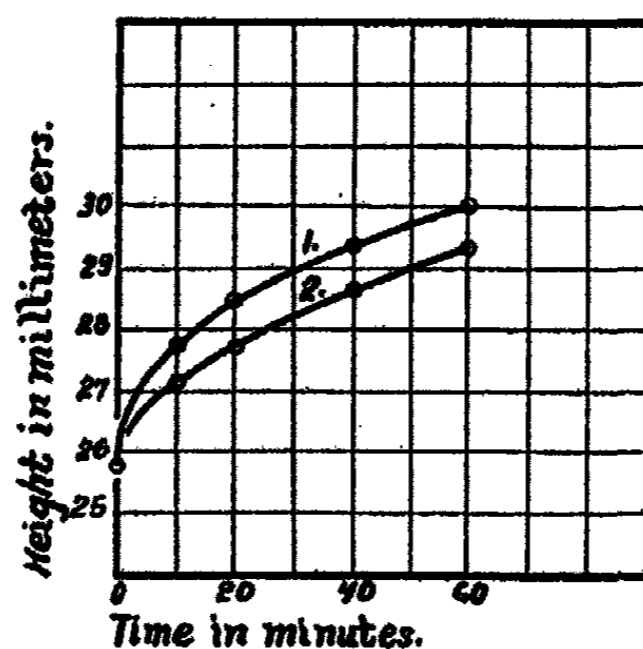


FIG. 7
Effect of sweeping away vapors.

side arm to carbon tetrachloride, causes a decrease in the height of the liquid in the capillary tube, at first; followed by a rise, as shown in B of Fig. 6. Evidently this rise is due to the dilution of the specifically heavier carbon tetrachloride by ether; resulting in a decrease in the weight of the column of liquid in the capillary tube. There is also further evidence that active mixing by convection such as has been described above goes on in these experiments; for carbon disulfide on distilling from the side tube to toluene causes, not a rise, as might be expected from its high surface tension; but a fall. Here the effect of its greater density is again apparent. This is shown in curve C of Fig. 6.

Effect of the Large Tube above the Capillary. The effect of the large tube above the capillary upon the rate of change of capillary height was next investigated, using a capillarimeter of type B and a solution which contained toluene and ether in equal proportions in terms of mol fraction. In the first experiment dry nitrogen was passed down the side arm of the capillarimeter and up the central large tube. The meniscus in the capillary tube was 11 mm. below its top. This gas current swept away the vapors coming from the capillary tube; and so, in effect, eliminated the tube above the capillary. The capillary height increased as shown in curve 1 of Fig. 3. Next the liquid

was drawn down, the capillary meniscus was re-formed, and an experiment was made without passing air. The capillary height increased as shown in curve 2 of Fig. 7. As will be seen, the rise is more rapid and more extensive when the vapors are swept away from the mouth of the capillary tube. The rate at which the gas is passed apparently does not influence the rate of rise, provided that it is not passed too slowly. This experiment was repeated with similar results using various pairs of liquids which gave, normally, a rise with time.

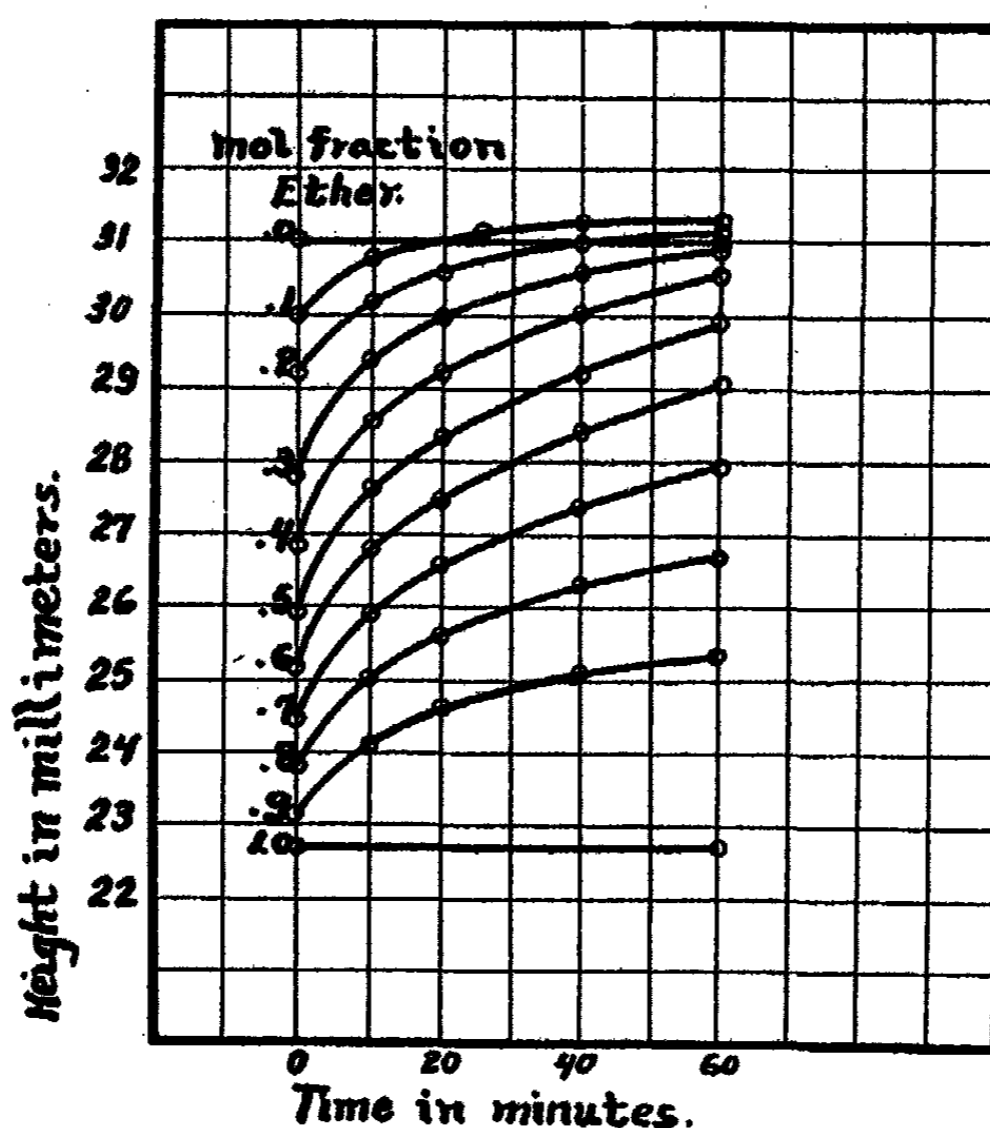


FIG. 8
Effect of concentration. Ether-toluene mixtures.

Another device for sweeping away the vapors from the mouth of the capillary tube and so, in effect, of eliminating the large tube, was found in capillarimeters of type C. When they were in use, the dried gas was passed through the side tube and up around the capillary, and so out. Reversing the direction of the gas current gave the same effect. These capillarimeters gave results which were much the same as those found with capillarimeters of type B.

It is very interesting to note that when the vapors are not swept away the rise of the liquid with time cannot be accurately represented by any of the simpler curves; but when they are swept away the rise with time during the first hour is represented closely by a parabola. This fact was established by

many experiments, using capillarimeters of both types, B and C. Its explanation is not immediately apparent. Evidently, however, for the best study of the alteration of capillary height with time for mixtures of liquids, the disturbing effect of a tube other than the capillary itself should be eliminated.

Effect of Concentration. The effect of the concentration of the more volatile component upon the rate of rise was then studied, using capillarimeters of type C. Mixtures of ether and toluene were again used, since, of all the pairs whose behavior has been studied, this one seemed to give the most consistent results. The changes for mixtures containing various concentrations of ether by mol fraction are set forth in the curves of Fig. 8. The numbers at the left indicate, in each case, the mol fraction of ether in the solution at the start. As will be seen, these curves are of the usual type. The rise is more rapid and more extensive for intermediate concentrations of ether. The fact that these mixtures, in two cases, showed greater capillary heights during the latter part of the experiment than did pure toluene, is to be explained as due to the fact that the mixtures at that time are specifically lighter than pure toluene. The tube length at the start of the experiment was 20 millimeters in every case.

Summary and Conclusions

Experiments, using the capillary rise method with mixtures of organic liquids confirmed the conclusion, reached by Washburn and Bigelow, that the variation of the surface tension of a mixture of liquids with time is due to preferential evaporation of the more volatile substance. The change which occurs may be a rise, a fall, or a rise succeeded by a fall of the column of liquid in the capillary tube. The rate and magnitude of the change depends upon the size and length of the capillary tube, being greater the less the tube length and the smaller the tube. If these factors are held constant, the nature of the change may be roughly predicted from a knowledge of the surface tensions, volatilities and densities of the components of the mixture. This work shows, again, that evaporation must be completely prevented if trustworthy data upon the surface tensions of mixtures, one or both of whose components is volatile, are to be obtained. This is, perhaps, the most important conclusion which can be drawn from the investigation.

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STRESS-STRAIN CURVES FOR PLASTIC SULFUR AND RAW RUBBER AT VARIOUS TEMPERATURES

BY JOHN D. STRONG

Introduction

A great deal of information regarding the elastic properties of a substance is revealed by its stress-strain curve. Materials which have very similar elastic properties should have stress-strain curves which have the same general shape and which change in the same manner with a change of temperature. Using the stress-strain curves as criteria to classify elastic substances, one would expect to find all types of substances from quartz on the one extreme to rubber on the other. There are no substances which would fall very near rubber in such a classification except, perhaps, the so-called plastic-sulfur.¹

It is the object of this research to establish the similarity of the elastic properties of raw rubber and plastic sulfur by the determination of stress-strain curves for each substance at various temperatures. These substances might be called "plastic-elastic" substances because they are neither purely elastic substances like quartz nor pure plastics like clay, but they exhibit some properties in common with both of these types of substances. A stress applied to either of these substances causes a reversible or elastic deformation and an irreversible or plastic deformation as well. This plastic deformation or plastic flow comes into most experiments, designed to show the elastic properties of these substances, to such an extent that their elastic properties cannot be brought clearly into focus.

In order to determine the true stress-strain diagrams of these substances, the plastic flow must be either measured and subtracted from the total extension in order to give the elastic deformation, or it must be eliminated. The ideal conditions for getting stress-strain data would be realized if the load could be applied instantly and if the elongation could be measured just after its application. Then there would be little time for plastic flow to occur. Practically, the closest approach to these conditions is to apply the load as rapidly as possible and determine the extension simultaneously with the application of the load. This means, that the testing machine must be equipped with an automatic recording device. The curves given in this paper were determined on machines that were equipped in this manner. The rate at which the load was applied was sufficiently rapid so that the errors introduced by plastic flow were judged to be of the same order of magnitude as the experimental errors due to other uncontrollable factors.

Experimental

Sulfur. Plastic sulfur filaments about 0.04" in diameter were prepared by pouring re-distilled sulfur which had been heated for some time at 300°C

¹ von Weimarn: Kolloid-Z., 6, 250 (1910). Elastischer kautschukartiger Schwefel.

into a cooling brine whose temperature was slightly below zero. By exercising care the plastic sulfur could be obtained in clear yellow filaments of surprising uniformity. Plastic sulfur prepared in this way was remarkably stable. Some filaments, immersed in water, retained their elastic properties for more than a day. It is unfortunate that the sulfur cannot be made to retain these useful properties permanently. If a means of "vulcanizing" and stabilizing plastic sulfur could be devised it might prove a worthy substitute for rubber especially since it costs but a few cents a pound.

The stress-strain data for sulfur were taken on a modified Jolly Balance (See Fig. 1). This machine was equipped to record automatically the applied load and the resulting extension.

Operation of Jolly Balance. Several turns of the filament about the sample hooks were made when the latter were in this zero position. The ends of the filament were then fixed. This gave a total length of 2.00 cm of filament per turn. The load and extension were automatically recorded by a curve traced with a pen. The record sheet and pen both move as the sample is tested. The sheet being attached to an aluminum plate, is raised vertically by turning the crank and thus the load is applied to the sample and a movement of the pen to the right occurs as the sample stretches. From the position of the pen at any instant both the load and corresponding extension may be determined. However, since the vertical motion of the sheet is shared between the extension of the sample and the extension of the load spring the extension of the sample must be taken into account before the load can be determined. In order to do this two empirical curves were plotted: first, the horizontal posi-

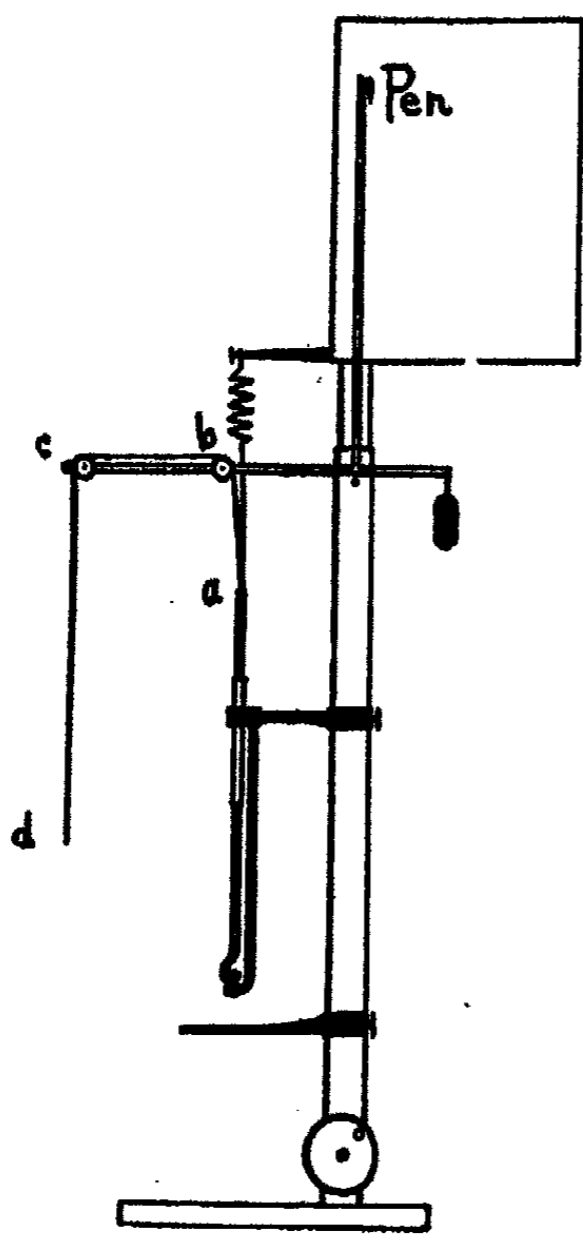


FIG. 1
Jolly Balance modified for Study of
Plastic Sulfur

tion of the pen (x) was plotted against the separation of the sample hooks under zero load, and second, the vertical position of the pen was plotted against the separation of the sample hooks under no load. As the sample was stretched, by turning the crank, the curve from which stress-strain data were determined was traced by the pen on the sheet. Three curves were traced at each temperature with similar sized samples. A curve was then constructed which was a mean of these curves. From this constructed curve the data

TABLE I

| Curve | A | | B | | C | |
|-------------------|-------------------------------------------------------------------|-----------|------------------------|-------------------------|-----------------------|-------------------------|
| | Temperature | Diameter | Temperature | Diameter | Temperature | Diameter |
| | -10.3°C | .0397 in. | -3.6°C | .0387 in. | +11.2°C | .0505 in. |
| Total cross Area | .01597 cm ² | | .03036 cm ² | | .0777 cm ² | |
| Modulus of Spring | 0.1014 Kg/cm | | 0.0841 Kg/cm | | 0.0841 Kg/cm | |
| | Extension | | | | | |
| Abcissa | Taken from an empirical curve of (x) vs. measured ext'n of sample | | | | | |
| X | 1 cm | 0.80 cm | 16.55 cm | 105 Kg/cm ² | 13.50 cm | 37.4 Kg/cm ² |
| 2 " | 1.60 " | 1.60 " | 19.30 " | 102.5 " | 15.90 " | 44.1 " |
| 3 " | 2.40 " | 2.40 " | 20.20 " | 128.0 " | 17.20 " | 47.7 " |
| 4 " | 3.15 " | 3.15 " | 20.65 " | 131.0 " | 18.00 " | 49.8 " |
| 5 " | 3.82 " | 3.82 " | 21.10 " | 134.0 " | 18.70 " | 51.8 " |
| 6 " | 4.45 " | 4.45 " | 21.30 " | 135.0 " | 19.45 " | 53.9 " |
| 7 " | 5.18 " | 5.18 " | 21.45 " | 136.0 " | 20.20 " | 56.0 " |
| 8 " | 5.83 " | 5.83 " | 21.50 " | 136.5 " | 20.85 " | 57.8 " |
| 9 " | 6.63 " | 6.63 " | 21.40 " | 135.9 " | 21.95 " | 60.8 " |
| 10 " | 7.35 " | 7.35 " | — | — | 23.05 " | 63.9 " |
| 11 " | 8.10 " | 8.10 " | — | — | 24.00 " | 66.5 " |
| 12 " | 8.80 " | 8.80 " | — | — | 24.90 " | 69.1 " |
| 9.70 " | 7.10 " | 7.10 " | 21.30 " | 135.2 " | — | — |
| 12.50 " | 9.10 " | 9.10 " | — | — | — | — |
| 12.55 " | 9.15 " | 9.15 " | — | — | — | — |
| | | | Ordnate | Stress | Ordnate | Stress |
| | | | Y ₀ -Y | Y ₀ -Y | Y ₀ -Y | Y ₀ -Y |
| | | | 4.85 cm | 5.25 Kg/cm ² | 4.85 cm | 5.25 Kg/cm ² |
| | | | 5.90 " | 6.40 " | 5.90 " | 6.40 " |
| | | | 6.55 " | 7.10 " | 6.55 " | 7.10 " |
| | | | 7.25 " | 7.85 " | 7.25 " | 7.85 " |
| | | | 7.75 " | 8.40 " | 7.75 " | 8.40 " |
| | | | 8.10 " | 8.77 " | 8.10 " | 8.77 " |
| | | | 8.55 " | 9.25 " | 8.55 " | 9.25 " |
| | | | 9.05 " | 9.80 " | 9.05 " | 9.80 " |
| | | | 9.60 " | 10.40 " | 9.60 " | 10.40 " |
| | | | 10.00 " | 10.83 " | 10.00 " | 10.83 " |
| | | | 10.50 " | 11.39 " | 10.50 " | 11.39 " |
| | | | 11.20 " | 12.12 " | 11.20 " | 12.12 " |
| | | | — | — | — | — |
| | | | 11.55 " | 12.50 " | 11.55 " | 12.50 " |

Eleven and one-half turns of the crank raise the aluminum plate 50 cm.
The rate at which the crank was turned was one-half revolution per second.

given in Table I were taken. $Y-Y_0$ is the total vertical displacement of the sheet minus the part of this displacement necessary to stretch the sample.

The two pulleys b and c are part of an arrangement for reducing the horizontal displacement of the pen caused by a given extension of the sample. The stress-strain curves plotted from these data appear in Fig. 2.

Rubber. The raw rubber was milled from smoked sheet stock into sheets approximately 50 mils in thickness. From these sheets narrow strips about 3.5 cm. long were cut and their ends were lapped and pressed together so that

they formed rings about 1 cm in diameter, (the splice being placed over one of the hooks which held the sample, when it was put in the machine to be tested).

Stress-strain data for rubber was taken on a modified Schopper Testing Machine (See Fig. 3). The load and extension were automatically recorded by a curve traced with a capillary pen on a sheet of paper. The angle, about the axis of the load arm, through which the pen is moved is a measure of the load applied to the sample. The difference between the angular deflection of the extension arm and the load arm is a measure of the extension of the sample. The pen is moved in toward the load arm axis by a silk thread running from the extension arm (a) over a pulley (b) to the pen (c). The movement of the pen toward the axis of the load arm is equal to the cord of this angular difference, but the cord is approximately equal to the arc for small angles, so that the movement of the pen toward the axis of the load arm was accordingly taken as proportional to the extension of the sample. The sample may be immersed in a cooling bath and tested while it is in this bath.

Samples of raw rubber were tested at -45°C , -55°C , -60°C , and -65°C . From the dimensions of the sample and the curve traced by the pen, the stress-strain curves were constructed. (See Fig. 4).

The absolute accuracy of this work is not claimed to be great since only small samples could be used. Some error was introduced due to the non-uniform stretching of the sample, since the portion of the sample behind the hook was no doubt restrained in its extension by friction against the hook. This particular error has, however, a similar effect on the stress-strain curves of both the rubber and the sulfur.

The maximum deviations of the stress as read from the constructed curve and as read from the most divergent of the curves traced by the Schopper

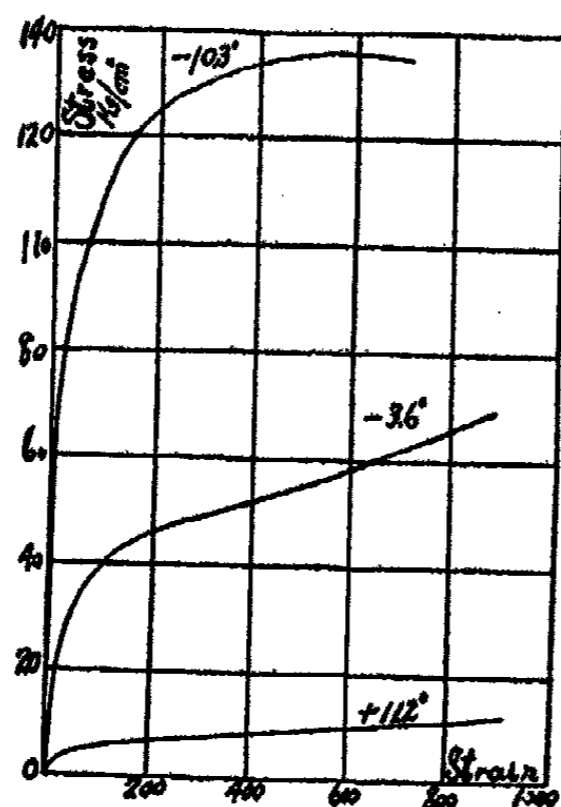


FIG. 2
Stress-strain Curves for Plastic Sulfur

Machine are: for A, 5%; for B, $4\frac{1}{2}$ %; for C, 7%. The average deviation of the diameter of the thread was about 2.5%. It does not seem unreasonable to estimate the probable error as 4%.

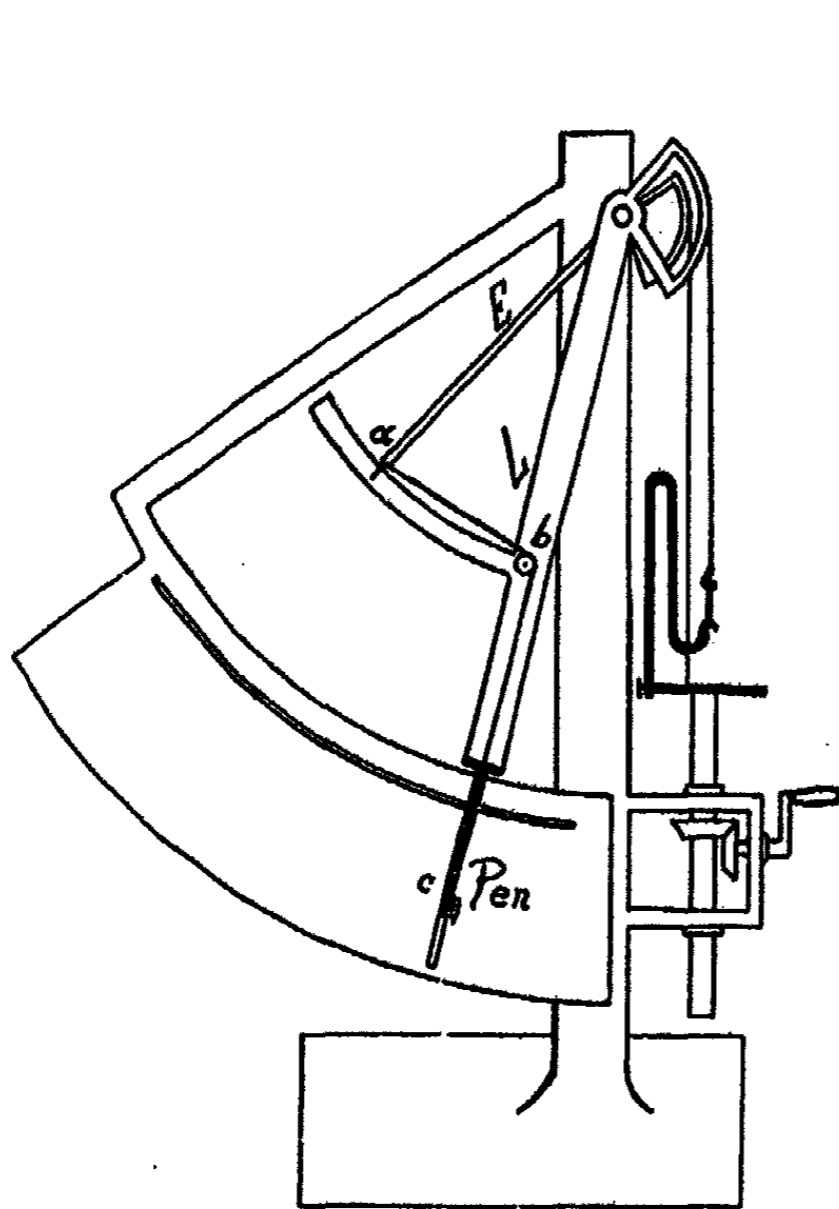


FIG. 3
Modified Schopper Machine

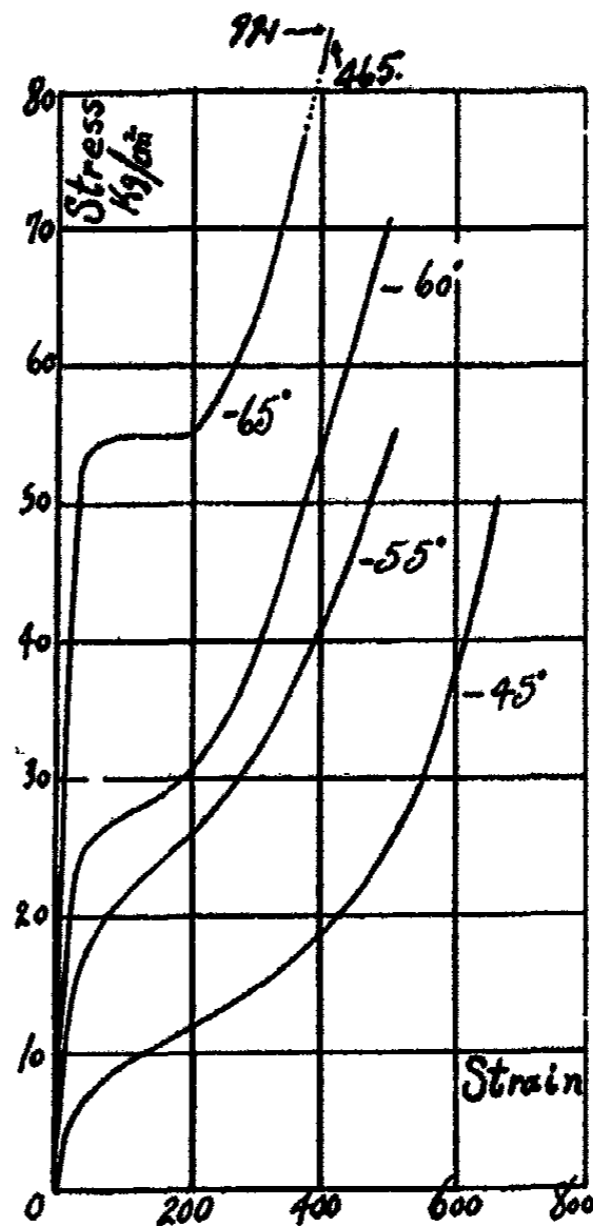


FIG. 4
Stress-strain Curves for Rubber

Discussion

It will be observed there is some little similarity between the stress-strain curves for the raw rubber and for plastic sulfur both in regard to their shape and the change of shape with temperature. The inflection point in the curve which is so characteristic for rubber is also distinctly present in the curve for sulfur taken at -3.6°C . No doubt the reason that this inflection point is not more marked is that the load per unit of "original" cross area is plotted as stress instead of the actual stress. If the actual stress were plotted the ordinates of the curve would be greater than shown by an amount directly proportional to the extension of the sample. This may also be given as an explanation of the retroflex portion of the sulfur curve taken at -10.3°C and of the flat portion at the inflection point of the raw rubber curve (the -60°C curve). This curve for rubber is very similar to a stress-strain curve for gutta

percha or balata at ordinary temperatures.¹ The curves for rubber given here do not agree quantitatively with the data given by Kröger and LeBlanc² in a paper "Vulcanization by Cooling". This discrepancy is no doubt due to the different rates of elongation.

Summary

The stress-strain curves of raw rubber and plastic sulfur are determined at various temperatures.

The stress-strain data were recorded automatically and this made possible a greater speed of testing. For this reason it is believed that the data are fairly independent of plastic flow.

Attention is drawn to the marked similarity between the stress-strain curves of raw rubber and plastic sulfur. If it had been possible to run either material on both testing machines this would have been done.

Schenectady, New York
August 26, 1927.

¹ Park: Ind. Eng. Chem., 17, 152 (1925).

² Kolloid-Z., 37, 206 (1925).

THE INFLUENCE OF CONCENTRATION OF A SOL ON ITS STABILITY

BY SUBODH GOBINDA CHAUDHURY

The effect of dilution of the colloid on the coagulating concentration of an electrolyte has been recognized long ago. Thus Woudstra¹ found that the greater the concentration of the colloid, the smaller the concentration of an electrolyte necessary to precipitate it. This is the reverse of what Freundlich² has observed with arsenious sulphide sols. Mukherjee and Sen³ observe (1) that the nature of the cation of the electrolyte and the extent of dilution determine whether the diluted sol is more or less stable than the original sol; and that (2) a diluted sol of arsenious sulphide is mostly more stable than the undiluted sol, when the precipitating cation is univalent, and always less stable when the cation is aluminium (trivalent) or thorium (tetravalent). When the cation is divalent either a diminution or an increase in stability may be observed. At moderate dilutions, the sol becomes unstable depending on the degree of dilution. Cupric and mercuric sulphide sols always showed an increase in stability on dilution. They have considered firstly the effect of decrease in the colloid-liquid interface which takes place on dilution and would under certain conditions diminish the stability and secondly an increase in the distance between the particles, i.e. the decrease in the number of particles in a given volume consequent on dilution, which adds to its stability. The observed effects are referred to the combined influence of these factors. Kruyt and van der Spek⁴ simultaneously came to similar conclusions.

A few years later Burton and his co-workers⁵ reported that for monovalent precipitating ions the concentration necessary for coagulation increases with dilution of the sol. In the case of divalent precipitating ions, values of coagulating power remain approximately the same in spite of the change in the concentration of the sol, whereas in the case of trivalent ions there is a direct proportionality between the concentration of the sol and the concentration of the precipitating ion. They postulated a relationship between the effect of dilution and the valency of the coagulating ions. From the observation of Mukherjee and Sen that a diminution or increase in stability is observed against coagulation by barium chloride depending on the extent of dilution, it is obvious that no such relationship can be postulated. The obvious explanation is that given by Mukherjee and Sen and by Kruyt and Spek. In a series of papers Dhar, Ghosh and Sen⁶ have studied the influence of the

¹ Z. physik. Chem., 61, 607 (1908).

² Z. physik. Chem., 44, 139 (1903).

³ J. Chem. Soc., 115, 461 (1919); see also J. Am. Chem. Soc., 37, 2024 (1915).

⁴ Kolloid-Z., 25, 1 (1919).

⁵ J. Phys. Chem., 24, 701 (1920); 25, 517 (1921).

⁶ J. Phys. Chem., 26, 701 (1922); 28, 313 (1924); 29, 435, 659 (1925); Kolloid-Z., 34, 262 (1924); 36, 219 (1925).

change of concentration of a sol on its coagulation and have formulated what they call a general dilution rule (Ghosh and Dhar) viz. that, the greater the dilution of a sol, the less is the amount of electrolyte necessary for coagulation, provided that the sol does not appreciably adsorb ions carrying the same charge as the sol from the coagulating electrolytes. On this basis they have classified these colloids into normal and abnormal ones¹. According to them normal colloids are those which follow this dilution rule. Those colloids which require a higher end concentration of the electrolyte for the coagulation of a more dilute sol are called abnormal colloids and they attribute the abnormality to the adsorption of similarly charged ions. That the similarly charged ions play a part in the coagulation of colloids has long been recognised by Freundlich² and Bancroft³. On considering the classification of these colloids into normal and abnormal ones, we find that there are cases where the so-called abnormal colloids show normal behaviour, e.g. As_2S_3 sol and $AgNO_3$ and also that normal colloids show abnormal behaviour, e.g. positively charged MnO_2 sol against $CuCl_2$ and $AgNO_3$. Examples might be multiplied. Thus we can at best speak of a normal and abnormal behaviour of colloids in the above sense. The above classification into normal and abnormal colloids is thus unjustifiable. The adsorption of the similarly charged ions was first given detailed attention by Weiser⁴ and he pointed out the fact that the influence of the ions having the same charge as the colloid cannot be disregarded entirely in any case and may be quite marked if the electrolyte precipitates the colloid at high concentration. From an investigation of the concentration of sols on their precipitation by electrolytes the following conclusions were formulated by Weiser⁵ in 1921.

(1) The manner in which the precipitating value of an electrolyte varies with the concentration of the colloid is determined to a large extent by the relative adsorbability of the precipitating ion and the stabilising ion.

(2) If the adsorption of the stabilising ion of an electrolyte is negligible and the adsorption of the precipitating ion is very large the precipitation value varies almost directly with the concentration.

Weiser⁶ in a recent communication observes: "Indeed Ghosh and Dhar found that the rule was followed with positive ferric oxide sol using potassium chloride but was abnormal if aluminium nitrate was the precipitating electrolyte. . . . Such a rule as Dhar has set down seems to me to be a positive menace rather than a help, if its limitations and the principles on which it is based are not recognised clearly". Regarding the experimental evidence for the statement that the adsorption of ions carrying the same charge as the particles increases on dilution, one finds only a single instance. The

¹ J. Phys. Chem., 31, 187, 666 (1927).

² "Kapillarchemie", 352 (1909); Z. physik. Chem., 44, 104 (1903).

³ J. Phys. Chem., 19, 363 (1915).

⁴ J. Phys. Chem., 24, 30 (1920).

⁵ Weiser and Nicholas: J. Phys. Chem., 25, 742 (1921).

⁶ J. Phys. Chem., 30, 20 (1926).

increase of the ratio of the adsorption of the similarly charged ion to that of the precipitating ion on dilution has been recorded in the case of positive MnO_2 sol and CuCl_2 (Ghosh and Dhar).

The chances of error in analytical measurements are very great and these experiments do not appear to be sufficiently convincing. Besides it has been pointed out by Mukherjee and Ghosh¹ that analytical measurements do not in reality give an idea of the type of the adsorption as would affect the charge but they give an idea of the exchange of ions between the double layer as a whole and the solution. In order to explain facts relating to coagulation with mixtures of electrolytes, Mukherjee and Ghosh have also been led to assume the adsorption of similarly charged ions. Electrical measurements of the charge of colloids under these conditions are necessary to throw further light on the subject. The author in a joint paper² has measured the variation of the rate of migration, i.e. the charge of colloidal particles, with dilution in the case of arsenious sulphide, copper ferrocyanide and gold sols. In each case it has been found that the charge of the colloidal solutions decreases on dilution. The data in Table I have been taken from the above paper. The rates have been corrected for viscosity taking that for water at the temperature as unity.

TABLE I

| As ₂ S ₃ sol | Temp. 35°C. |
|---------------------------------------------------------------------------|-------------------------------------------------|
| Dilution in ratio of volume of original sol to that of water added to it. | Rate of migration in cms. per sec. per volt/cm. |
| Pure sol | 60.1×10^{-5} |
| 1 : 1 | 58.9×10^{-5} |
| 1 : 3 | 55.7×10^{-5} |
| 1 : 10 | 17.5×10^{-5} |
| 1 : 20 | 12.2×10^{-5} |

All the previous workers in this field have overlooked the possibility of the decrease of the charge with dilution in the case of at least some colloids, which would tend to sensitise the sol on dilution against electrolytes. The question naturally arises whether the relative increase in adsorption of the similarly charged ion suffices to counteract the decrease in charge on dilution. Measurements of the charge of colloids diluted and undiluted, keeping the electrolyte concentration the same, were done three years back³. The data were taken with arsenious sulphide sol and hydrochloric acid.

TABLE II

| c.c. of stock colloid | c.c. of water | Dilution | c.c. of N/25 HCl | Mobility at 30° in cm. per sec. per volt per cm. |
|-----------------------|---------------|----------|------------------|--------------------------------------------------|
| 25 | nil | 1 | 25 | 38.9×10^{-5} |
| 15 | 10 | 1.66 | 25 | 38.9×10^{-5} |
| 10 | 15 | 2.5 | 25 | 39.1×10^{-5} |

¹ J. Indian Chem. Soc., 1, 213 (1924).

² Mukherjee, Chaudhury and Roy Chaudhury: Quart. J. Indian Chem. Soc.

³ J. Chem. Soc., 125, 79 (1924).

It seems likely from these results that the relative adsorption of anions increases, since the colloid without any electrolyte shows a decrease in its charge on dilution. But the increased adsorption does not increase the charge sufficiently to make it stable towards univalent electrolytes in the case of As_2S_3 sol, for the values are very nearly equal. We are therefore forced to the conclusion that greater distance between the colloidal particles in a diluted sol is at least partly if not mostly responsible for stabilisation against monovalent electrolytes in the case of As_2S_3 sol.

In a recent paper Ghosh and Dhar¹ write "that the view advanced by Kruyt and Spek and by Mukherjee and Sen that the decreased chance of collision amongst the colloidal particles is an important factor that prevents a weaker sol of As_2S_3 from coagulating is not corroborated by experiment." The experimental data given here show that the relative increase in the adsorption of anions alone is not sufficient to make the sol stable on dilution but that the increase in the distance of the colloidal particles on dilution is equally, if not more, potent in bringing about stabilisation. This, it seems to the author, has been experimentally proved from the data given in this paper. Ghosh and Dhar forget that the particles must meet together before they can agglomerate into bigger particles, and the rate of such collision must be taken into consideration. The mean distance between the particles determines among other factors the number of such collisions. The point need not be pressed further in view of the classical works of Smoluchowski² and of Zsigmondy³.

The observations up to date on the variation of the coagulating concentration of different electrolytes on dilution of the colloid might be fully accounted for in the following manner:—

On diluting a colloid, both the charge and the total surface of the colloidal particles decrease, whereas the distance between the particles increases. Diminution of charge and also of the total surface tend to make the sol unstable against coagulation by electrolytes *provided it is assumed that the potential at which a sol coagulates does not change on diluting the sol and that the relative adsorption of all ions on the surface remains the same*. The greater distance between the particles of a diluted sol tends to make it more stable. That in a number of cases, the sol becomes unstable on dilution, is presumably due to preponderance on the first two effects over the third. Now when the ratio of the amount of adsorption of similarly charged ions to that of the precipitating ions increases, we meet with another factor that tends to make it more stable on dilution. The increased adsorption may be attributed to one or more of the following possibilities:

- (a) A relative increase in the adsorbability of the similarly charged ions.

¹ J. Phys. Chem., 31, 649 (1927).

² Z. physik. Chem., 92, 129 (1917).

³ Z. physik. Chem., 92, 500 (1918); see also Mukherjee and Papaconstantinou: Phil. Mag., 44, 302 (1922); Hatschek, Mukherjee and Mazumdar: J. Chem. Soc., 125, 785 (1924); Anderson; Gammer and Lewis.

(b) Increase in the equilibrium concentration of the electrolyte consequent on the decrease in the colloid-liquid interface. In this case it will be necessary to assume further that with the increase in concentration the relative adsorption of the similarly charged ions increases.

The second possibility may be neglected, for in general we have found that the manner of variation of the charge with the concentration of electrolyte does not warrant this assumption. The adsorption theory of Freundlich predicts that dilution of the sol will always diminish its stability and in the limiting case of univalent salts, this theoretical diminution may not be perceptible. Diminution of charge on dilution shows that a consequent change takes place on the surface of the colloidal particles, on dilution, and probably this is the reason why relative adsorbability also changes with dilution. It is also possible on the views of adsorption of similarly charged ions put forward by Mukherjee¹ to attribute the increased relative adsorption of the similarly charged ions to a diminution in the charge itself, which increases considerably the number of collisions of the similarly charged ions on the surface, assuming that the concentration of these ions remains constant. The main reason for the difference in the behaviour of a colloid on dilution against coagulation by electrolytes—which as we have seen above depends on the nature of the coagulating electrolyte—is perhaps to be sought in the difference in the coagulating concentrations. When the concentration is high, the effect of diminution of interface on dilution is negligible, and the increased distance between the particles has a dominating influence. The reverse is the case when the coagulating concentration is very low. In the present paper, we have in the absence of relevant charge measurements assumed that coagulation always takes place at a definite potential of the double layer for the same sol. This is not always true, as would appear from the measurements of Mukherjee and Chaudhury² and Mukherjee, Chaudhury and Roy Chaudhury³.

My thanks are due to Prof. J. N. Mukherjee, D.Sc., for his kind interest in the subject.

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¹ Phil. Mag., 44, 321 (1922).

² J. Indian Chem. Soc., 2, 296 (1926).

³ Communicated for publication.

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THE SYSTEM CALCIUM OXIDE, SILICA AND WATER

BY JOHN R. BAYLIS

The chemical literature contains very little on the hydrated calcium silicates, though there have appeared within the past few years several articles on sodium silicate and a number of articles on the characteristics of silica gel. The importance of the reaction between calcium oxide and silica cannot be overestimated, for portland cement constitutes one of the most extensively used building materials. Mixtures of lime and sand have been used in the building of masonry structures for thousand of years and while there may be some doubt as to whether or not the lime reacts with the silica in the surface of the sand grains the evidence is in favor of the reaction though it be very slow. Certainly there is a reaction when the temperature is near the boiling point of water. Very little cement, which is largely composed of calcium oxide and silica, was used until the latter part of the eighteenth century, and practically all the famous cathedrals, fortresses and other masonry structures of the middle ages used common lime mortar for the joints.

Natural cements, made by burning a clayey material, came into use about 1800 and reached their maximum output between 1890 and 1900. Portland cement was invented in 1825, but production in the United States did not extend rapidly until after 1880. Approximately 164,530,000 barrels of portland cement were produced in 1926. Lime mortar (mixture of hydrated lime and silica sand) is still a very extensively used cementing material. It is known that portland cement involves reactions between calcium oxide and silica and it is believed that this is also the case with lime mortar. If this is true for lime mortar, then the value of new structures being built which involves at least the partial holding together of the materials with some cementing material dependent largely or partially on the reaction between calcium oxide and silica probably exceeds three billion dollars annually in the United States alone. Such a sum should make this chemical reaction one of great importance.

The classical work of Patrick and his collaborators¹ on silica gel and Harman² on aqueous solutions of sodium silicates, now give a very good understanding of many of the characteristics of silica, and of its sodium compounds. Even though the reactions between calcium oxide and silica in the presence of water are probably of much greater importance, due to the exten-

¹ Patrick and McGavack: *J. Am. Chem. Soc.*, 42, 946, 976 (1920); Neuhausen and Patrick: *J. Phys. Chem.*, 25, 693 (1921); Patrick and Grimm: *J. Am. Chem. Soc.*, 43, 2144 (1921); Patrick and Jones: *J. Phys. Chem.*, 29, 1 (1925); Davidheiser and Patrick: *J. Am. Chem. Soc.*, 44, 1 (1922); Patrick and Eberman: *J. Phys. Chem.*, 29, 220; Patrick and Lorn: 336; Patrick, Preston and Owen: 419; Patrick and Opdyke: 601; Patrick and Greider: 1031; Patrick and Barclay: 1400 (1925); Patrick, Frazier and Rush: *J. Phys. Chem.*, 31, 1511 (1927).

² R. W. Harman: *J. Phys. Chem.*, 29, 1155 (1925); 30, 359, 917, 1100 (1926); 31, 335, 511, 616 (1927).

sive use of cementing materials, etc., there appears to be very little about them in the literature. Much has been written on portland cement clinker, but very little on the hydration of the cement compounds. At the time of this writing there has appeared an article by Lerch and Bogue¹ giving some information on the hydrolysis of compounds of calcium and silica likely to occur in portland cement. This article will be discussed more fully in the latter part of the paper.

To obtain information on the equilibrium of mixtures of calcium hydroxide, silica and water, experiments, varying the amount of calcium hydroxide in solution in the presence of compounds of silica such as the hydrous oxides of silica, have been conducted. The results indicate that there may be a definite chemical reaction between calcium hydroxide and the hydrous oxides of silica forming a compound closely approaching to CaO , SiO_2 . In addition to this, considerable calcium hydroxide appears to be adsorbed by this compound when the concentration of calcium hydroxide in the surrounding solution is increased over that necessary to form the definite compound.

Preparation of the Silica

Dilute solutions of pure sodium silicate (water glass) were treated with hydrochloric acid until the alkali was completely neutralized, except in one instance where it was treated to where the solution showed only a slight pink color when phenolphthalein was added. Various dilutions of the sodium silicate were used and jellies of various textures were formed, from the very stiff one that formed immediately on the addition of the acid to the very dilute solution that required over 24 hours for the jelly to form. The jellies were placed in Pyrex flasks and distilled water added. They were broken up fairly fine by agitating the mixture and mashing up the lumps with a plunger. The broken-up jellies were allowed to settle and the clear solution poured off. The procedure of adding distilled water and pouring off the supernatant liquid after the precipitate had settled was continued until the solution, after standing in contact with the precipitate for several days, showed only a few parts per million of Cl_2 .

The washing, in the case where the alkali was not completely neutralized, was then continued for 11 months with various periods of standing between washings of from one day to a month or more. It was hoped that the precipitate could be washed free from the alkali, but the process was so slow that this was abandoned. For this particular jelly, which was used in Experiment 1, both sodium hydroxide and soluble sodium silicate were being given off in the solution at the last washing.

In one instance the jelly was dried before the salt was washed out, first at about 90°C , then at about 110° for 6 hours. The dried gel was placed in a flask and washed in the same manner as the jellies until practically free from chlorides. It was then dried for 24 hours at a temperature of approximately 130°C . The dried gel contained 3.31 percent water.

¹ Lerch and Bogue: *J. Phys. Chem.*, 31, 1627 (1927).

Experiments adding Calcium Oxide

The experiments will be numbered, though not in the order conducted. Unless otherwise stated, the CaO given in the tables and shown on the curves is the actual CaO. The lime usually tested about 99 percent CaO.

Experiment 1. A siliceous jelly containing approximately 10 grams of SiO_2 in which the sodium was not completely neutralized.

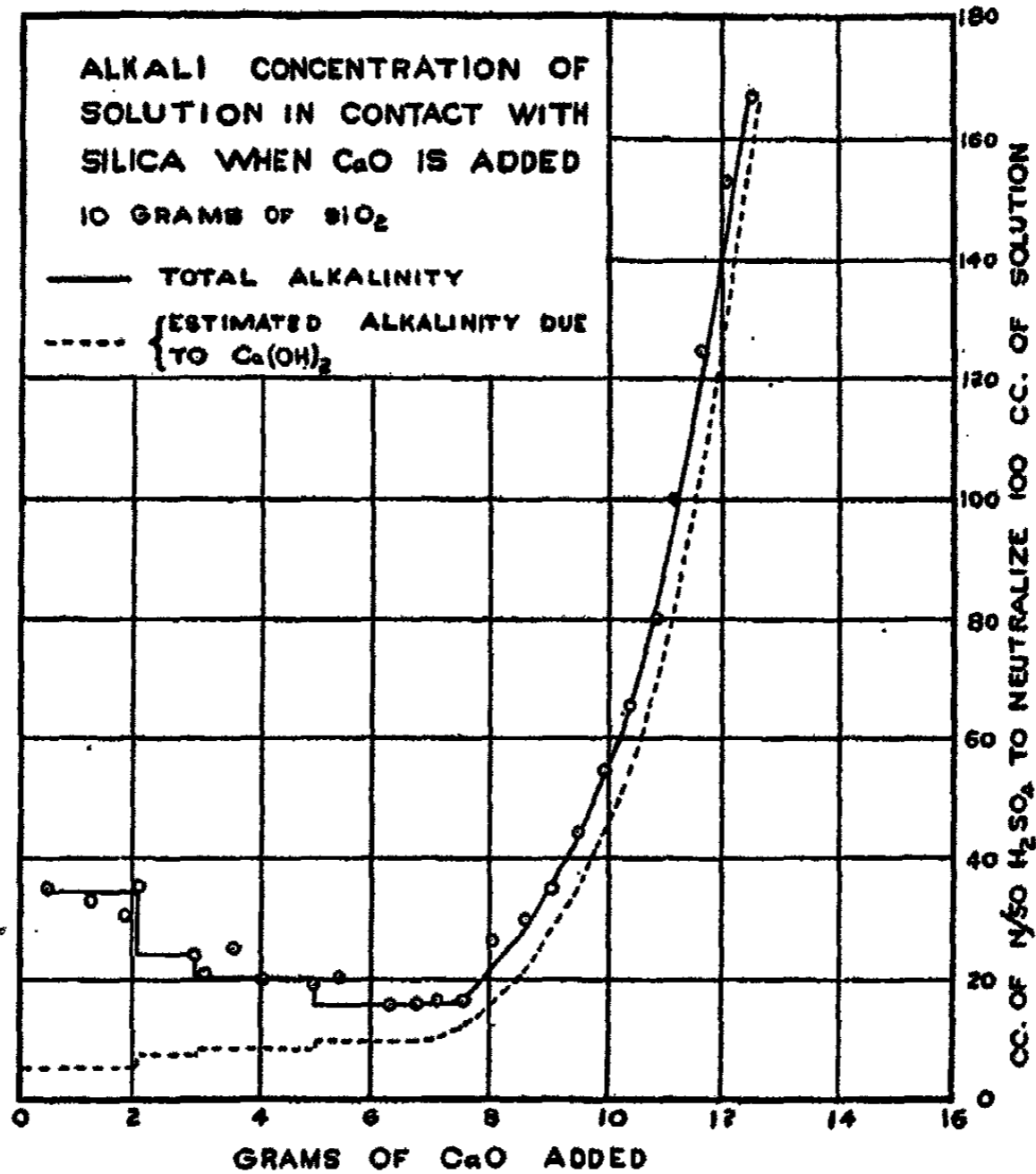


FIG. 1

The jelly was placed in a 300 cc. Pyrex flask and the flask filled to the 300 cc. mark with distilled water. There is doubt as to the exact amount of silica used in this experiment. It was estimated by evaporating a measured portion of the precipitate to dryness and then determining the SiO_2 by the usual gravimetric method. It is difficult to get a measured portion of a solution containing a precipitate in which the precipitate is uniformly distributed. In this test there was no other way of approximating the silica.

Calcium oxide was then added in small weighed quantities and the mixture thoroughly agitated after each addition of the calcium. The flask contained a steel ball about $\frac{5}{8}$ inch in diameter for grinding up any lumps that

TABLE I

Alkali Concentration of Solution in Contact with Silica with Various Quantities of CaO added

| Total CaO added Grams | Days standing | Phenolphthalein | Methyl Orange | cc. of N/50 H ₂ SO ₄ to neutralize 100 cc. of the solution |
|-------------------------------------------------------------|---------------|-----------------|---------------|----------------------------------------------------------------------------------|
| 0.00 | 104 | 12.2 | 18.6 | |
| .54 | 1 | 32.0 | 35.0 | |
| 1.26 | 1 | 31.0 | 33.0 | |
| 1.80 | 1 | 31.0 | 31.4 | |
| 2.16 | 2 | 33.0 | 36.0 | |
| 200 cc. of distilled water added to make up amount removed. | | | | |
| 2.88 | 1 | 22.0 | 24.0 | |
| 200 cc. of distilled water added to make up amount removed. | | | | |
| 3.24 | 4 | 19.0 | 22.0 | |
| 3.60 | 1 | 23.0 | 25.0 | |
| 4.05 | 1 | 18.0 | 20.0 | |
| 4.95 | 1 | 16.0 | 18.0 | |
| 200 cc. of distilled water added to make up amount removed. | | | | |
| 5.40 | 1 | 19.0 | 21.0 | |
| 6.30 | 1 | 14.0 | 16.0 | |
| 6.75 | 1 | 15.0 | 17.0 | |
| 7.20 | 1 | 15.0 | 17.0 | |
| 7.65 | 1 | 15.0 | 17.0 | |
| 8.10 | 3 hrs. | 25.0 | 27.0 | |
| 8.55 | 1 day | 28.0 | 30.0 | |
| 9.00 | 1 | 33.0 | 35.0 | |
| 9.45 | 1 | 43.0 | 45.0 | |
| 200 cc. of distilled water added to make up amount removed. | | | | |
| 9.90 | 1 | 53.0 | 55.0 | |
| 10.35 | 1 | 64.0 | 66.0 | |
| 10.80 | 1 | 78.0 | 80.0 | |
| 11.25 | 1 | 99.0 | 101.0 | |
| 11.70 | 1 | 122.0 | 124.0 | |
| 12.15 | 1 | 151.0 | 153.0 | |
| 12.60 | 1 | 191.0 | 194.0 | |
| | 4 | 171.0 | 174.0 | |

formed. The agitation was continued at frequent intervals throughout the day. The usual procedure was to add 0.45 grams of CaO daily. Small portions, usually 10 cc., of the clear liquid were withdrawn and tested with a standard acid after the addition of each quantity of lime. In fact the test was made just before adding the next portion of lime. Four times during the process of adding the lime, 200 cc. of distilled water were added to make up that removed for testing. This gives the jumps shown in the first part of the curves in Fig. 1. It is assumed that the calcium replaced the sodium in combination with or adsorbed by the silica in the early stages of the addition of the lime and that most of the alkali in solution at first was sodium hydroxide and sodium silicate. Each addition of distilled water reduced the concentration of the sodium hydroxide, and it is assumed that the curves should make abrupt breaks at these points though it may be somewhat overdrawn in the figure. From the fact that the alkali concentration of the solution, especially the estimated $\text{Ca}(\text{OH})_2$ concentration, remained low until most of the lime was added, it may be concluded that not much of the calcium was lost in the solution removed for testing.

The curves in Fig. 1 show the alkali concentration of the solution and the amount that was estimated to be calcium hydroxide. These curves are plotted without taking into consideration any losses such as the amount of calcium in the solution removed for testing and in the solution within the flask, and while they are slightly in error they are so nearly correct that for the intended purpose of the curves this is of little consequence. It will be noted that the alkali concentration of the solution remained low until about 8 grams of CaO had been added, and then began to increase. This would seem to indicate a definite compound being formed up to this point, although the proportions do not altogether correspond with the theoretical requirements to form CaO, SiO_2 if 10 grams of SiO_2 were actually in the flask. The calcium silicate is, of course, in the hydrated form. This seems to be a characteristic of the fairly stiff jellies as will be shown later. The figures used in plotting the solid line curve in Fig. 1 are given in Table I.

Testing the solution for sodium after the last addition of calcium showed it to contain about 50 parts per million of Na. Unfortunately, no tests for soluble silica were made as the calcium was being added. According to other experiments it must have been fairly high at first, but very low near the end of the test. The table gives the number of cc. of acid solution required to neutralize 100 cc. of the solution. As a matter of fact only 10 to 25 cc. of the solution were used for most of the tests.

After the addition of 16.20 grams of CaO, a portion of the precipitate was removed for chemical analysis. This is given in Table II.

TABLE II

| Chemical Analysis of Precipitate | | | |
|----------------------------------|-------------|-------------------------|-------------|
| SiO_2 | .4384 grams | Fe_2O_3 | .0011 grams |
| CaO | .5013 " | Al_2O_3 | .0043 " |
| SO_2 | .0040 " | MgO | .0041 " |

Experiment 2. The silica gel was prepared in the usual manner, except that HCl was added until the jelly showed a slight red color with methyl orange. This was a pH of about 4.0.

The pH at the end of the washing was 5.5. The amount of silica was estimated in two ways. The first estimate was made before any calcium was added. This was done by taking a measured portion of the stirred-up

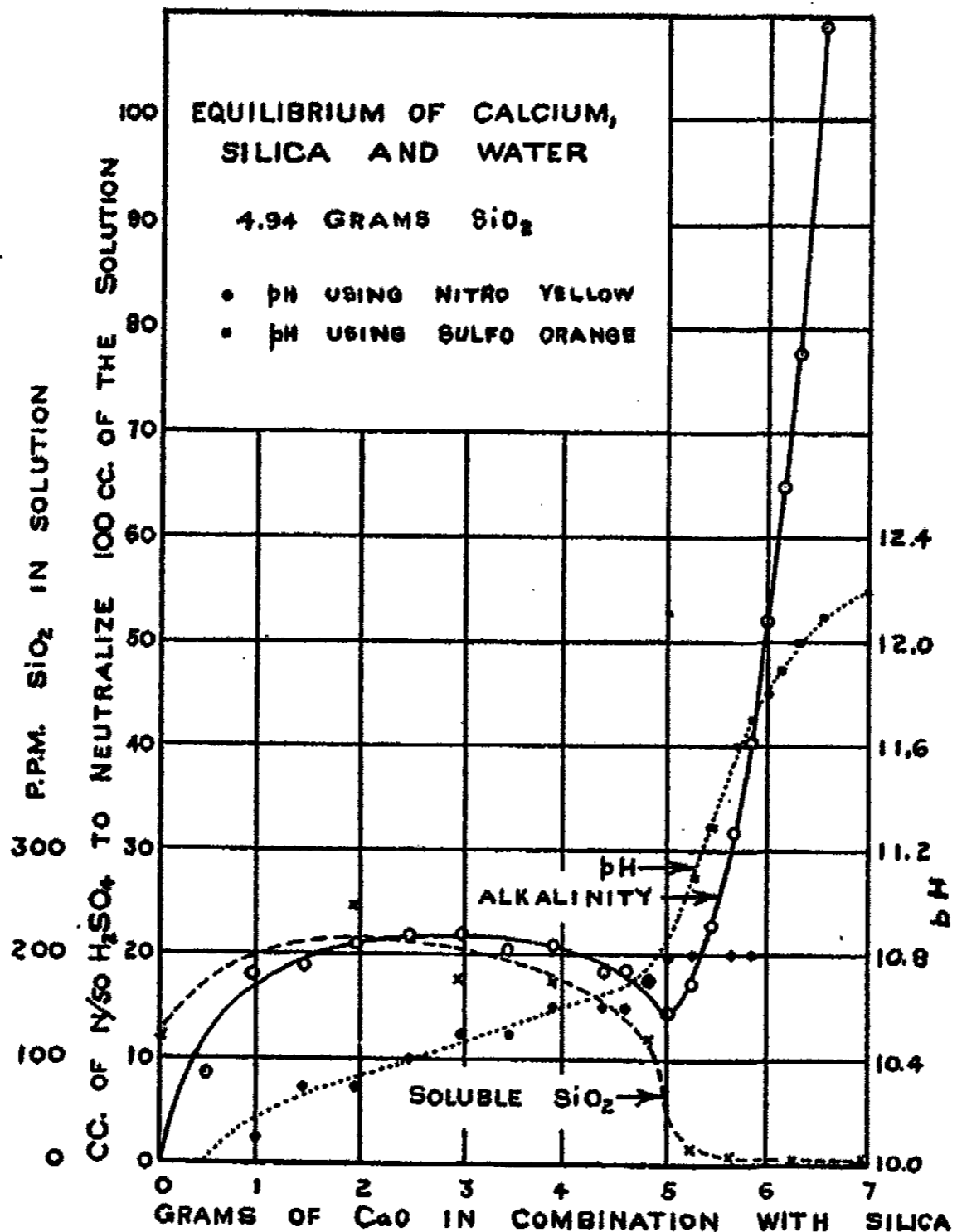


FIG. 2

precipitate and determining the silica gravimetrically. The computed SiO_2 for the silica remaining in the flask was 4.94 grams. At the end of the experiment the entire precipitate was dried, weighed, ground fine, and a chemical analysis made of a weighed portion of the ground powder. This is shown in Table IV. From this analysis the SiO_2 remaining at the end of the test was estimated to be 4.61 grams. Considering the silica removed in the solution for testing the two analyses probably check very well. 4.61 grams of

SiO_2 require 4.28 grams of CaO to form CaO, SiO_2 . It will be noted from the alkalinity curve in Fig. 2 that there is a minimum point, or drop in the curve, where approximately 5 grams of CaO is estimated to be in chemical combination with the silica. Experiment 1 showed that less CaO than the theoretical was required to reach this point of drop in the alkalinity curve.

It may be well to call attention to the fact that the dilution of the sodium silicate before precipitating the jelly was fully twice as much for the jelly used in Experiment 2 as in Experiment 1. There is some evidence that this is the reason, which if true, it may be that the calcium hydroxide had difficulty in penetrating to the interior of some of the particles of jelly. In Experiment 2 there appears to be slightly more calcium hydroxide in combination to reach the low point of alkali in solution than the theoretical necessary to form CaO, SiO_2 . Small quantities of iron and aluminum oxides (approximately 2 percent of the SiO_2) were present, which would account for a small quantity of the excess calcium. Due to the large number of tests in which the flask had to be opened to withdraw samples, there, no doubt, was a carbonation of another small quantity of the calcium. There is, however, no proof that the minimum alkalinity point occurs at the point where there is complete conversion of the silica to calcium silicate, even though it is believed to be near this point.

Everything has been taken into consideration in Experiment 2; that is, deductions have been made for the calcium removed in the samples of the solution used for testing and for the calcium that was in solution. The points shown on the curves in Fig. 2 and given in Table III represent the calcium oxide actually in chemical combination with, or adsorbed by the silica. Two to three days were allowed for the solution to reach equilibrium before the next addition of calcium oxide. The figures given in the table do not comprise all the tests made, but only those made just before the next addition of calcium. The usual procedure was to make pH and alkalinity tests, 4 hours, 24 hours and 48 to 72 hours after the addition of each quantity of calcium. Equilibrium was nearly established within 4 hours, consequently there can be little doubt as to the adequacy of the time allowed. The sample was agitated 15 to 20 times each day and as the volume of the precipitate was about one-half the total volume of the sample it is evident that the solution had ample opportunity to come in contact with the solid matter.

The pH is only approximate. It was determined with standards prepared by the LaMotte Chemical Products Co., but there is some doubt as to their accuracy. Where the color ranges of nitro yellow and sulfo orange, which were the indicators used, should overlap there is a difference in the pH as determined with the two indicators. Several years ago the writer attempted to use the hydrogen electrode for making pH determinations on calcium hydroxide solutions. The notes made at the time showed a pH of 12.35 for a saturated solution of calcium hydroxide at room temperature, which averaged about 23 degrees C. Upon returning the electrode to a buffered solution it was always off considerably. The opinion was formed that the hydrogen

electrode was not very accurate for strong calcium hydroxide solutions. The pH results, however, agree very well with those obtained by others and may be correct. Largely from the fear of the unreliability of the pH determinations none were made for the first experiments.

It is yet believed that a better conception of the equilibrium is obtained from titrating with a standard acid solution when the calcium hydroxide concentration is fairly high. In Table III are given both the phenolphthalein and methyl orange alkalinities but only the methyl orange alkalinity is shown in Fig. 2. Perhaps the pH gives the better interpretation of the experiment for the first part of the curves where there is considerable calcium silicate in solution. The monocalcium silicate in solution, if there be such a compound present, is broken down at a pH that still gives a slightly pink color when phenolphthalein is present; that is, the phenolphthalein alkalinity also includes practically all of the alkali in the soluble calcium silicate.

TABLE III
Equilibrium of Calcium Hydroxide, Silica and Water
Silica gel containing approximately 4.94 grams of SiO_2 —
Volume of water with precipitate kept constant at 1 liter

| Total CaO added Grams | CaO estimated to be in combination with and adsorbed by the Silica Grams | cc. of N/50 H_2SO_4 to neutralize 100 cc. of the solution | | pH | P.P.M. of SiO_2 passing the Filter Papers |
|-----------------------------|--------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|------------------|-----------|----------------------------------------------------------------|
| | | Phenol- phthalein | Methyl Orange | | |
| .495 | .494 | 8.0 | 9.5 | 10.0 | |
| .990 | .988 | 16.5 | 18.5 | 10.1 | |
| 1.485 | 1.480 | 17.0 | 19.0 | 10.3 | |
| 1.980 | 1.968 | 19.0 | 21.0 | 10.3 | 240 |
| 2.475 | 2.440 | 20.0 | 22.0 | 10.4 | |
| 2.970 | 2.930 | 19.5 | 22.0 | 10.5 | 172 |
| 3.465 | 3.404 | 18.5 | 20.5 | 10.5 | |
| 3.960 | 2.893 | 19.0 | 21.0 | 10.6 | 172 |
| 4.455 | 4.370 | 17.0 | 18.5 | 10.6 | |
| 4.702 | 4.610 | 17.0 | 18.5 | 10.6 | |
| 4.950 | 4.850 | 16.0 | 17.5 | 10.7 | 120 |
| 5.197 | 5.002 | 12.5 | 14.0 | 10.8 | |
| 5.445 | 5.222 | 15.5 | 17.0 | 10.8-11.1 | 16 |
| 5.692 | 5.431 | 22.0 | 23.0 | 10.8-11.3 | |
| 5.940 | 5.623 | 30.5 | 31.5 | 10.8-11.6 | 9 |
| 6.187 | 5.792 | 39.5 | 40.5 | 11.7 | |
| 6.435 | 5.962 | 50.5 | 52.0 | 11.8 | |
| 6.682 | 6.111 | 64.0 | 65.0 | 11.9 | |
| 6.930 | 6.272 | 76.0 | 78.0 | 12.0 | 2 |
| 7.425 | 6.494 | 105.0 | 107.0 | 12.0 | |
| 7.920 | 6.712 | 151.0 | 152.0 | 12.1 | |
| 8.910 | 7.078 | 218.5 | 221.5 | 12.2 | 2 |

Nitro Yellow

Sulfo Orange

A correct interpretation of the curves in Fig. 2 would be difficult. The solutions were filtered through two thicknesses of No. 40 Whatman filter paper before making the silica determinations. It is quite probable that some of the silica passing was not in solution. It will be noted that a content of over 100 parts per million of SiO_2 was found in the filtrate before any calcium hydroxide had been added. It is not believed that silica, under the conditions of the experiment, is so soluble. The silica in solution, if any, may exist partially in the dissociated state. The fact that a prolonged washing of one sample of the silica jelly prepared similarly to that used in this experiment continued to show a few parts per million of alkalinity and a pH above 7.0 after being washed free from chlorides, indicates either the presence of an adsorbed alkali or else that the soluble silica is at least partially dissociated and that the dissociated product gives a pH near or slightly above 7.0.

The addition of calcium oxide to a solution in which there is a gelatinous precipitate of a hydrous oxide of silica forms a slightly soluble calcium silicate, the exact amount in solution being difficult to determine. This increases the silica passing the filter papers. As to whether the increase is practically all in solution or not, and is represented by the difference between that passing before calcium hydroxide is added and afterwards, there was no way of determining with the equipment at hand. At any rate, the soluble silica in this experiment reached a maximum when about 2 grams of CaO had been added. This was at a pH of about 10.3 with the indicator used (nitro yellow).

The continued addition of calcium hydroxide increases the pH and reduces the amount of silica that will pass the filter papers. When nearly 5 grams of CaO had entered into combination there was a marked drop in the amount of silica passing the filter papers. This is also coincident with a drop in the amount of acid solution necessary to neutralize the solution. The peak in the alkalinity curve when 2 to 3 grams of CaO had been added is due probably to some free calcium hydroxide, some soluble calcium silicate and some of the silica passing in the colloidal state carrying alkali with it. It is possible, though there is no proof in the experiment as conducted, that compounds of lesser calcium content than CaO , SiO_2 are formed. It is also possible that the solid silica holds part or nearly all the calcium by adsorption rather than by definite chemical combination.

The addition of a weak solution of HCl to particles of the precipitate after all the calcium has been added dissolves the calcium from the particles without disturbing to a noticeable extent the shape of the particles, indicating that the structural formation of the jelly is not altered by the addition or removal of the calcium. Proof of this is readily obtained by observing particles under the microscope in a cell through which a weak acid solution is passed. This phenomenon may be significant, especially as the density of the jelly formed in precipitating the silica seems to influence the amount of calcium that will enter into combination with or be adsorbed by the silica.

After a pH of about 11.0 is reached, as determined by the somewhat unsatisfactory method used, very little soluble silica remains and the calcium hydroxide concentration of the solution then increases fairly rapidly upon the

addition of more calcium oxide. Beyond this point there is not enough silica in solution to materially affect the results, and the equilibrium between the solid silicate in whatever state it exists and the calcium hydroxide in solution appears to be one of surface adsorption. Beyond the five-gram point in Fig. 2 the alkalinity curve agrees with the Freundlich adsorption equation. It also will be shown that this equilibrium is reversible, another factor strongly indicating adsorption. Approximately 30 to 45 percent as much calcium is taken up by what is believed to be adsorption, when the calcium hydroxide concentration of the solution is increased to the saturation point, as is required to bring it to the point where rapid increase in the alkali concentration of the solution started. In other words, it required in this experiment approximately 5 grams of CaO to reach the point where the alkali concentration of the solution started up fairly rapidly, but between this point and the saturation point of calcium hydroxide approximately 2 grams of calcium oxide went into some kind of combination with the solid silicates.

Perhaps the most convincing proof of the above is the analysis of the precipitate at the end of the test. The entire content of the flask was filtered, washed with an amount of distilled water about 50 percent in excess of the volume of the precipitate to wash away approximately an equal amount of the calcium hydroxide as remained in the solution in the gelatinous precipitate, then dried at 100 degrees C. The total weight of the dried precipitate was 22.16 grams. Chemical analysis of the precipitate is given in Table IV.

TABLE IV
Analysis of One Gram of the Dried Precipitate and the Computed CaO and SiO₂ present in the Total Precipitate

| | |
|---------------------------------------------------------------------------------------------|---------------------|
| Silicon dioxide (SiO ₂) | .2082 grams |
| Calcium oxide (CaO) | .3054 " |
| Iron and aluminum oxides (Fe ₂ O ₃ , Al ₂ O ₃) | .0045 " |
| Not determined | .0053 " |
| Loss on ignition | .4766 " |
| | <u>1.0000</u> grams |

Chemical analysis was checked by a second analysis.

| | |
|-------------------------------------------------------------------------|------------|
| Estimated SiO ₂ in total sample (22.16 × .2082) | 4.61 grams |
| Estimated CaO in total sample (22.16 × .3054) | 6.77 " |
| CaO added in excess of the saturation point | .20 " |
| Total CaO in combination with silica, iron, aluminum and carbon dioxide | 6.57 " |

It is believed that the amount of calcium oxide in combination with compounds other than the silica is less than 0.20 gram. This would leave at least 6.37 grams in combination with and adsorbed by the silica, or 48.8 percent more calcium oxide than was necessary to combine with the silica to form CaO, SiO₂. While this figure may not be absolutely correct it is believed to

be only slightly in error and not enough to materially affect the result. Taking the figures given in Table III and computing the excess calcium oxide after taking into consideration the probable amount of calcium carbonated it figures about 50 per cent in excess of the theoretical necessary to form $\text{CaO}\cdot\text{SiO}_2$.

Experiment 3. Concentrated silica jelly.

The silica jelly was prepared in the same general manner as for the other experiments, except that the concentration of silica was much greater. This formed a very stiff jelly immediately on adding the acid. The pH after the addition of the acid was 5.0, and at the end of the washing it was 7.2. The jelly was placed in a 500 cc. Pyrex flask and the water kept at a constant volume of 500 cc. Table V gives the results of the addition of CaO to the flask.

TABLE V
Equilibrium of Calcium Hydroxide, Silica and Water
The silica jelly contained approximately 9.30 grams SiO_2 .
The volume of the jelly before the addition of water was 120 cc.

| Total CaO added Grams | CaO estimated to be in combination with and adsorbed by the Silica Grams | cc. of N/50 H_2SO_4 to neutralize 100 cc. of the solution | | pH | P.P.M. of SiO_2 passing the Filter Papers |
|--------------------------------|--------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|------------------|------|----------------------------------------------------------------|
| | | Phenol- phthalein | Methyl Orange | | |
| 4.95 | 4.894 | 18.0 | 20.0 | 10.3 | |
| 6.93 | 6.897 | 10.0 | 11.0 | 11.0 | 65 |
| 7.92 | 7.849 | 20.5 | 21.5 | 11.5 | 13 |
| 8.91 | 8.737 | 48.0 | 50.0 | 11.8 | |
| 9.90 | 9.571 | 99.0 | 100.0 | 12.0 | |
| 10.89 | 10.337 | 172.0 | 174.0 | 12.2 | |

This experiment shows approximately the same results as Experiments 1 and 2. All losses of CaO and silica are taken into consideration in the table. The lime was added to the flask very much faster than for the other experiments to hasten the completion of the experiment. It is not believed that this had a material influence on the results. At the end of the experiment all the precipitate was filtered out, washed with a volume of distilled water about 50 per cent greater than the volume of the precipitate, dried, weighed, and a portion analyzed. This is shown in Table VI.

TABLE VI
Chemical Analysis of Dried Precipitate from Experiment 3

| | |
|--------------------------------------------------------------------------------|--------------|
| Silicon dioxide (SiO_2) | .2900 grams |
| Calcium oxide (CaO) | .3305 " |
| Iron and aluminum oxides (Fe_2O_3 , Al_2O_3) | .0041 " |
| Loss on ignition | .3600 " |
| Unaccounted for | .0154 " |
| | <hr/> |
| | 1.0000 grams |

It will be noted from the analysis that there was a higher amount unaccounted for than should have been the case. The error probably was in determining the loss on ignition, for the other analyses were checked. This, however, does not affect the calcium-silica ratio. It will be noted that there is a lesser quantity of CaO per gram of silica in combination and adsorbed than in Experiment 2. Also, it will be noted that while less CaO than the theoretical to form CaO, SiO_2 was required to reach the point where the rapid increase in the calcium hydroxide concentration of the solution starts, the CaO going into combination or adsorbed beyond this point is not so greatly different from that in Experiments 1 and 2. This would indicate that the concentration of the silica in the jelly influenced the amount of calcium hydroxide going into combination to form monocalcium silicate more than it does the calcium hydroxide adsorbed, if we are justified in assuming that monocalcium silicate is formed and that adsorption starts at the point where the rapid increase in the calcium hydroxide concentration of the solution starts.

Experiment 4. Very dilute jelly.

There is nothing about Experiment 4 greatly different from the other experiments, except that as much water as would allow a jelly to form within 2 days was added. The pH after the addition of the acid was about 5.0, and was 6.4 at the end of the washing. Table VII gives the results of the addition of CaO. The volume of water with the precipitate was kept constant at 2 liters.

TABLE VII
Equilibrium of Calcium Hydroxide, Silica and Water
The silica jelly contained approximately 8.22 grams of SiO_2 .
The volume of the jelly before the addition of water was 950 cc.

| Total CaO added Grams | CaO estimated to be in combination with and adsorbed by the Silica Grams | cc. of N/50 H_2SO_4 to neutralize 100 cc. of the solution | | pH | P.P.M. of SiO_2 passing the Filter Paper |
|--------------------------------|--------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|------------------|------|---------------------------------------------------------------|
| | | Phenol- phthalein | Methyl Orange | | |
| 5.94 | 5.716 | 18.0 | 20.0 | 10.5 | |
| 7.92 | 7.684 | 18.0 | 19.0 | 11.3 | 13 |
| 8.91 | 8.422 | 38.0 | 39.5 | 11.7 | |
| 9.90 | 9.084 | 67.0 | 68.0 | 11.9 | |
| 10.89 | 9.659 | 102.5 | 104.0 | 12.0 | |
| 11.88 | 10.186 | 143.0 | 144.0 | 12.2 | |
| 12.87 | 10.667 | 185.0 | 188.0 | 12.2 | |

While enough points were not determined to draw accurate curves as was done for Experiment 2, it is evident from the few results given that the curves would follow those shown in Fig. 2 very closely. It is also noted that the minimum point of alkalinity, except at the beginning of the experiment, is near the theoretical to form CaO, SiO_2 , which, in this case, is 7.63 grams of

CaO. 10.67 grams of CaO was estimated to be in combination with and adsorbed by the silica at the last addition of calcium, which was slightly below the saturation point. Drawing a curve and projecting it on to the saturation point 10.82 grams of CaO is obtained. This is 41.8 percent more calcium oxide than the theoretical necessary to combine with 8.22 grams of SiO₂, the amount of silica found to be present in the flask at the end of the experiment. Table VIII shows the chemical analysis of the precipitate at the end of the experiment.

TABLE VIII

| | 1 | 2 |
|------------------------------------------------------------------------------------------------|-------------|-------------|
| Silicon dioxide (SiO ₂) | .1900 Grams | .1838 Grams |
| Calcium oxide (CaO) | .2450 " | .2378 " |
| Iron and aluminum oxides (Fe ₂ O ₃ , Al ₂ O ₃) | .0016 " | .0015 " |

Experiment 5. Dried silica gel.

The sodium silicate was neutralized with hydrochloric acid, dried, washed free from chlorides, again dried, and then weighed. It was dried at approximately 130 degrees C for 6 hours, which left only 3.31 percent water. A portion of the pulverized gel containing 7.735 grams of SiO₂ was placed in a 500 cc. Pyrex flask and the flask filled to the 500 cc. mark with distilled water. The results of the addition of calcium oxide are given in Table IX.

TABLE IX

Equilibrium of Calcium Hydroxide, Silica Gel and Water

| Total CaO added Grams | CaO estimated to be in combination with and adsorbed by the Silica Grams | cc. of N/50 H ₂ SO ₄ to neutralize 100 cc. of the solution | | pH | P.P.M. of SiO ₂ passing the Filter Papers |
|--------------------------------|--------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|------------------|------|------------------------------------------------------------------|
| | | Phenol- phthalein | Methyl Orange | | |
| .495 | .493 | 18.0 | 20.0 | 10.2 | |
| .990 | .933 | 17.0 | 19.0 | 10.3 | 243 |
| 1.485 | 1.410 | 17.0 | 19.0 | 10.3 | |
| 1.980 | 1.898 | 17.5 | 19.0 | 10.4 | 226 |
| 2.970 | 2.876 | 16.0 | 17.0 | 10.3 | |
| 3.960 | 3.864 | 13.0 | 14.0 | 10.3 | 150 |
| 4.950 | 4.844 | 12.0 | 13.0 | 10.7 | |
| 5.940 | 5.829 | 15.0 | 16.0 | 11.2 | 11 |
| 6.930 | 6.693 | 45.0 | 46.0 | 11.8 | |
| 7.920 | 7.487 | 108.0 | 110.0 | 12.0 | |
| 8.910 | 8.272 | 171.0 | 173.0 | 12.2 | |
| 9.405 | 8.634 | 200.0 | 202.0 | 12.2 | |

This sample of silica behaved in the experiment very much like the jellies, except that it required a longer time to reach equilibrium after each addition of the calcium oxide. The volume of the precipitate was quite small at first,

but increased considerably as the lime was being added though not to equal that of any of the jellies. The gel was made from a fairly stiff jelly (1 gram of SiO_2 to 20 cc. water) and the CaO entering into combination and adsorbed was approximately the same as that for the other fairly stiff jellies. Some silica was lost in the solution removed for testing and 7.74 grams of SiO_2 were estimated to be present at the end of the test.

Experiments Indicate Adsorption

Every experiment where a jelly of the pure hydrous oxide of silica had been formed shows that the silica will unite with more CaO than the theoretical to form CaO,SiO_2 . Table X gives a summary of the 5 experiments.

TABLE X

| Exp. No. | cc. of water per gram of SiO_2 | SiO_2 at the End of Test Grams | CaO in combination and adsorbed when the solution is saturated with CaO Grams | Theoretical CaO to form SiO_2 Grams | CaO per gram SiO_2 | Percent CaO in excess of CaO,SiO_2 |
|----------|-----------------------------------------|-----------------------------------------|-------------------------------------------------------------------------------|----------------------------------------------|-----------------------------|----------------------------------------------------|
| 1 | 35 | 10.00 | 12.60 | 9.28 | 1.26 | 35.8 |
| 2 | 75 | 4.61 | 6.37 | 4.28 | 1.38 | 48.8 |
| 3 | 14 | 9.30 | 10.74 | 8.64 | 1.15 | 24.3 |
| 4 | 95 | 8.22 | 10.82 | 7.63 | 1.32 | 41.8 |
| 5 | 20* | 7.64 | 8.75 | 7.10 | 1.14 | 21.6 |

* Volume of jelly before drying.

The nature of the jelly seems to have some influence on the amount of CaO that it will unite with, but all experiments show the same characteristics. A careful examination of Fig. 2, which is typical for all the experiments, leaves little room for doubting that there is adsorption of the calcium hydroxide. It indicates but does not give positive proof that monocalcium silicate is the definite compound formed. There is no indication whatever of the formation of dicalcium silicate, nor is there enough calcium taken up to account for such a compound. Several extraction tests were run to show that the calcium hydroxide is given off in the same general manner in which it is adsorbed.

Extraction of Calcium Hydroxide from Calcium Silicate

If the assumption of adsorption of calcium hydroxide by calcium silicate is correct the equilibrium must be reversible; that is, the calcium hydroxide must be given off in the same proportion in which it is adsorbed. Extraction tests were made on several samples of calcium silicate that had reached equilibrium in solutions containing a high concentration of calcium hydroxide by withdrawing the clear liquid above the precipitate, replacing with distilled water, and repeating the procedure after equilibrium had been established. In these experiments it was impossible to avoid removing a small

amount of the precipitate each time, and even though the amount was very small, a large number of extraction tests no doubt removes a fairly large amount of the precipitate. Using distilled water that contained 3 to 4 parts per million of CO_2 carbonated a little of the calcium hydroxide. If all these losses could be determined it is believed that the extraction tests would be almost exactly in the reverse order of the tests where calcium oxide was added.

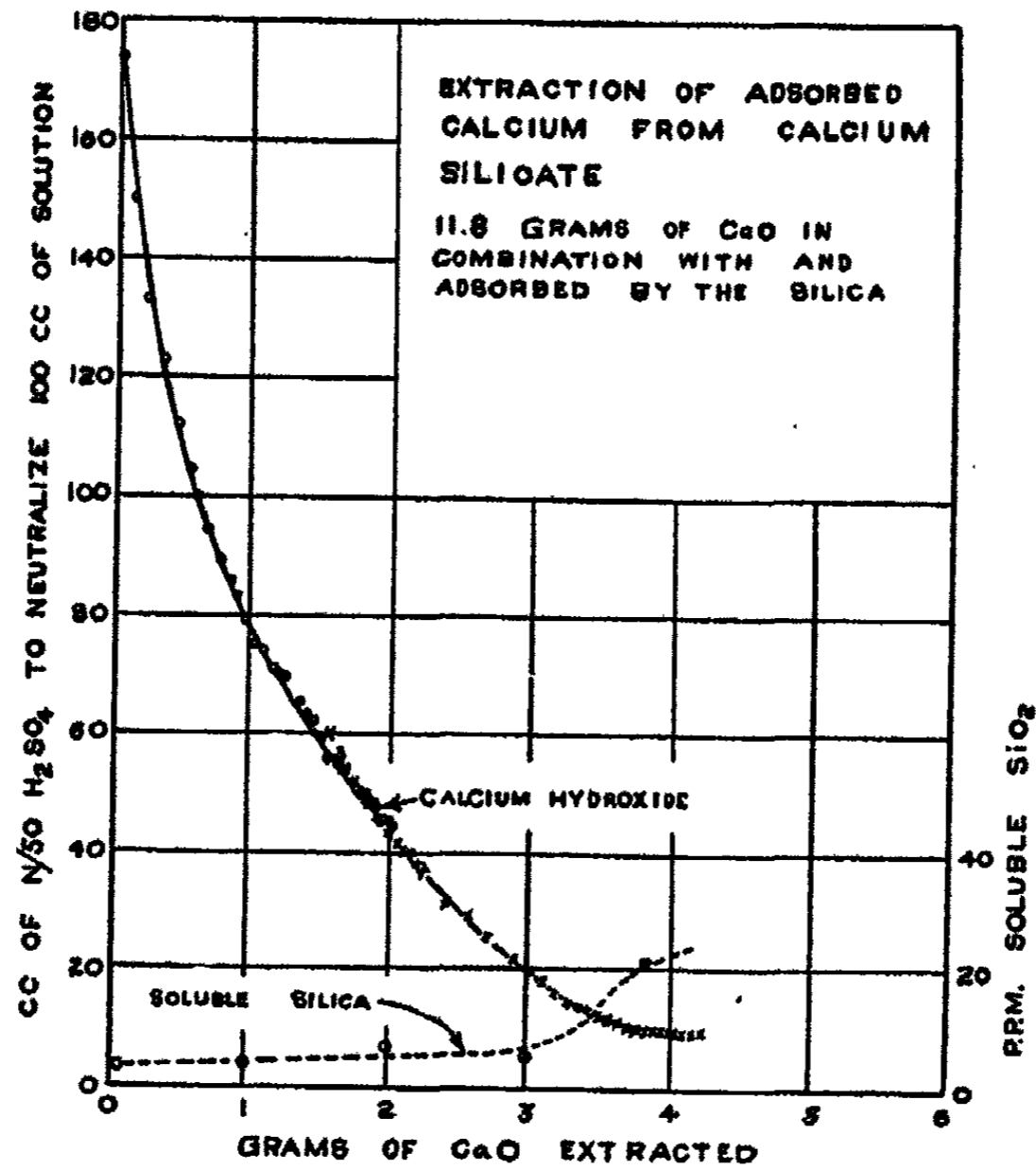


FIG. 3

Extraction Experiment 1. This was the precipitate from Experiment 1 where CaO was added to a gelatinous precipitate of silica. This also was after the precipitate shown by the analysis in Table II was removed.

The procedure of the extraction tests was to withdraw and test a measured portion of the clear solution after standing over night without agitation. The results are given in Table XI and are also shown by the curve in Fig. 3. It is evident that all the points given in the table could not be shown on so small a scale as that of Fig. 3. For tests standing longer than one day the sample was agitated several times each day. The flask was filled to the 300 cc. mark each time after withdrawing the quantities given in Table XI, except when the tests show a removal of 200 cc., in which case the flask was

filled nearly full or to the 350 cc. mark. This means that there was a dilution of at least 50 percent at each test when 150 cc. were removed, and a slightly greater dilution when 200 cc. were removed.

TABLE XI

Extraction of Adsorbed Calcium from Calcium Silicate

This is the precipitate from Experiment 1, less a small amount removed for analysis.

| Days standing | cc. of solution withdrawn | cc. of N/50 H ₂ SO ₄ to neutralize 100 cc. of the solution | | Estimated CaO Grams | Total CaO extracted Grams | Soluble Silica P.P.M. SiO ₂ |
|---------------|---------------------------|----------------------------------------------------------------------------------|---------------|---------------------|---------------------------|----------------------------------------|
| | | Phenolphthalein | Methyl Orange | | | |
| 1 | 150 | 150.0 | 152.0 | .128 | .128 | 5.0* |
| 1 | 150 | 132.0 | 134.0 | .113 | .241 | |
| 1 | 150 | 121.0 | 124.0 | .104 | .345 | |
| 1 | 150 | 110.0 | 113.0 | .095 | .440 | |
| 1 | 150 | 104.0 | 106.0 | .089 | .529 | |
| 1 | 150 | 98.0 | 100.0 | .084 | .613 | |
| 1 | 150 | 92.0 | 94.0 | .079 | .692 | |
| 1 | 150 | 87.0 | 89.0 | .075 | .767 | |
| 1 | 150 | 84.0 | 86.0 | .072 | .839 | |
| 4 | 150 | 81.0 | 83.0 | .070 | .909 | |
| 1 | 150 | 76.0 | 78.0 | .066 | .975 | 5.0* |
| 1 | 150 | 73.0 | 75.0 | .063 | 1.038 | |
| 1 | 150 | 72.0 | 74.0 | .062 | 1.100 | |
| 1 | 150 | 69.0 | 71.0 | .060 | 1.160 | |
| 1 | 150 | 68.0 | 70.0 | .059 | 1.219 | |
| 3 | 150 | 68.0 | 70.0 | .059 | 1.278 | |
| 1 | 150 | 63.0 | 65.0 | .055 | 1.333 | |
| 1 | 150 | 61.0 | 63.0 | .053 | 1.386 | |
| 1 | 150 | 59.9 | 62.0 | .052 | 1.438 | |
| 1 | 190 | 56.0 | 58.0 | .062 | 1.500 | |
| 1 | 200 | 54.0 | 56.0 | .063 | 1.563 | |
| 1 | | 53.0 | 55.0 | | | |
| 3 | | 54.0 | 55.5 | | | |
| 5 | 200 | 54.0 | 56.0 | .063 | 1.626 | |
| 1 | 200 | 52.0 | 54.0 | .061 | 1.687 | |
| 1 | 200 | 50.0 | 52.0 | .058 | 1.745 | |
| 1 | 200 | 48.5 | 50.5 | .057 | 1.802 | |
| 1 | 200 | 46.0 | 48.0 | .054 | 1.856 | |
| 2 | 200 | 46.5 | 48.0 | .054 | 1.910 | |
| 1 | 200 | 44.0 | 45.5 | .051 | 1.961 | |
| 1 | 200 | 42.0 | 44.0 | .049 | 2.010 | |

At this point 0.45 grams of CaO was added to the flask and the sample thoroughly agitated. The 0.45 gram is subtracted from the total CaO extracted.

TABLE XI (Continued)
cc. of N/50 H₂SO₄
to neutralize 100 cc.
of the solution

| Days standing | cc. of solution withdrawn | Phenolphthalein | Methyl Orange | Estimated CaO Grams | Total CaO extracted Grams | Soluble Silica P.P.M. SiO ₂ |
|---------------|---------------------------|-----------------|---------------|---------------------|---------------------------|----------------------------------------|
| 2 | | 58.0 | 60.5 | | 1.560 | |
| 1 | 200 | 55.5 | 57.0 | .064 | 1.624 | |
| 1 | 200 | 53.5 | 55.0 | .062 | 1.686 | |
| 1 | 200 | 50.0 | 52.0 | .058 | 1.800 | |
| 1 | 200 | 48.0 | 50.0 | .056 | 1.800 | |
| 1 | 200 | 46.0 | 48.0 | .054 | 1.854 | |
| 1 | 200 | 44.0 | 45.5 | .051 | 1.905 | |
| 3 | 200 | 44.5 | 46.5 | .052 | 1.957 | |
| 3 | | 43.0 | 45.0 | | | |
| 11 | | 43.5 | 45.5 | | | |
| 18 | | 43.5 | 45.5 | | | |
| 24 | 200 | 43.5 | 45.5 | .051 | 2.008 | |
| 1 | 200 | 42.0 | 44.0 | .049 | 2.057 | 5.5* |
| 1 | 200 | 38.5 | 40.5 | .045 | 2.102 | |
| 1 | 200 | 37.0 | 39.0 | .044 | 2.146 | |
| 1 | 200 | 37.2 | 38.8 | .043 | 2.189 | |
| 1 | 200 | 36.2 | 38.0 | .043 | 2.232 | |
| 1 | 200 | 34.8 | 36.4 | .041 | 2.273 | |
| 1 | 200 | 34.0 | 35.2 | .039 | 2.312 | |
| 1 | 200 | 32.4 | 33.6 | .037 | 2.347 | |
| 1 | 200 | 31.6 | 32.6 | .037 | 2.386 | |
| 1 | 200 | 30.0 | 31.2 | .035 | 2.421 | |
| 1 | 200 | 29.4 | 31.0 | .035 | 2.456 | |
| 1 | 200 | 28.2 | 30.4 | .034 | 2.490 | |
| 1 | 200 | 28.0 | 29.8 | .033 | 2.523 | |
| 1 | 200 | 28.0 | 29.6 | .033 | 2.556 | |
| 1 | 175 | 27.9 | 28.8 | .027 | 2.583 | |
| 1 | 200 | 27.2 | 28.4 | .032 | 2.615 | |
| 1 | 200 | 26.4 | 27.6 | .031 | 2.646 | |
| 1 | 200 | 26.0 | 27.4 | .031 | 2.677 | |
| 1 | 200 | 25.0 | 26.4 | .029 | 2.706 | |
| 1 | 200 | 24.8 | 26.0 | .029 | 2.735 | |
| 1 | 200 | 24.0 | 25.2 | .028 | 2.763 | |
| 1 | 200 | 23.6 | 24.6 | .028 | 2.797 | |
| 1 | 200 | 22.4 | 23.8 | .027 | 2.818 | |

TABLE XI (Continued)

| Days standing | cc. of solution withdrawn | cc. of N/50 H ₂ SO ₄ to neutralize 100 cc. of the solution | | Estimated CaO Grams | Total CaO extracted Grams | Soluble Silica P.P.M. SiO ₂ |
|---------------|---------------------------|----------------------------------------------------------------------------------|---------------|---------------------|---------------------------|----------------------------------------|
| | | Phenolphthalein | Methyl Orange | | | |
| I | 200 | 21.6 | 23.2 | .026 | 2.844 | |
| I | 200 | 21.4 | 22.8 | .026 | 2.870 | |
| I | 200 | 20.8 | 22.0 | .025 | 2.895 | |
| I | 200 | 21.0 | 22.0 | .025 | 2.920 | 5.5 |
| I | 200 | 20.0 | 21.2 | .024 | 2.944 | |
| I | 200 | 20.0 | 21.2 | .024 | 2.986 | |
| I | 200 | 19.6 | 20.4 | .023 | 2.991 | |
| I | 200 | 18.8 | 19.6 | .022 | 3.013 | |
| I | 200 | 18.4 | 19.2 | .021 | 3.034 | |
| I | 200 | 18.0 | 19.2 | .022 | 3.056 | |
| I | 200 | 17.2 | 18.8 | .021 | 3.077 | |
| I | 200 | 16.8 | 18.8 | .021 | 3.098 | |
| I | 200 | 16.0 | 18.0 | .020 | 3.118 | |
| I | 200 | 16.0 | 17.8 | .020 | 3.138 | |
| I | 200 | 16.0 | 17.6 | .020 | 3.158 | |
| I | 200 | 15.6 | 16.8 | .019 | 3.177 | |
| I | 200 | 15.2 | 16.8 | .019 | 3.196 | |
| I | 200 | 15.6 | 16.8 | .019 | 3.215 | |
| I | 200 | 15.2 | 16.8 | .019 | 3.234 | |
| I | 200 | 14.4 | 15.6 | .017 | 3.251 | |
| I | 200 | 14.0 | 15.6 | .017 | 3.268 | |
| I | 200 | 14.4 | 15.6 | .017 | 3.285 | |
| I | 200 | 14.0 | 14.8 | .017 | 3.302 | |
| I | 200 | 13.6 | 14.8 | .016 | 3.318 | |
| I | 200 | 13.2 | 14.4 | .016 | 3.334 | |
| I | 200 | 12.4 | 13.0 | .015 | 3.349 | |
| I | 200 | 12.0 | 14.0 | .015 | 3.364 | |
| I | 200 | 12.8 | 14.0 | .016 | 3.380 | |
| I | 200 | 12.4 | 14.0 | .016 | 3.396 | |
| I | 200 | 12.8 | 14.8 | .016 | 3.412 | |
| I | 200 | 12.4 | 14.0 | .016 | 3.428 | |
| I | 200 | 12.0 | 13.6 | .015 | 3.443 | |
| I | 200 | 11.6 | 13.2 | .015 | 3.458 | |
| 2 | 200 | 11.2 | 12.8 | .014 | 3.472 | |
| I | 200 | 11.6 | 12.8 | .014 | 3.846 | |

TABLE XI (Continued)

| Days standing | cc. of solution withdrawn | cc. of N/50 H ₂ SO ₄ to neutralise 100 cc. of the solution | | Estimated CaO Grams | Total CaO extracted Grams | Soluble Silica P.P.M. SiO ₂ |
|---------------|---------------------------|----------------------------------------------------------------------------------|---------------|---------------------|---------------------------|----------------------------------------|
| | | Phenolphthalein | Methyl Orange | | | |
| I | 200 | 11.2 | 12.8 | .014 | 3.500 | |
| I | 200 | 11.2 | 12.8 | .014 | 3.514 | |
| I | 200 | 11.2 | 12.4 | .014 | 3.528 | |
| I | 200 | 10.8 | 12.4 | .013 | 3.541 | |
| 7 | 200 | 10.8 | 12.0 | .013 | 3.554 | |
| 18 | 200 | 10.8 | 12.4 | .014 | 3.568 | |
| I | 200 | 10.8 | 12.0 | .013 | 3.581 | |
| 3 | 200 | 10.0 | 12.0 | .013 | 3.594 | |
| I | 200 | 10.8 | 12.0 | .013 | 3.607 | |
| I | 200 | 10.0 | 12.0 | .013 | 3.620 | |
| 2 | 200 | 10.0 | 11.6 | .013 | 3.633 | |
| I | 200 | 10.0 | 11.6 | .013 | 3.646 | |
| I | 200 | 10.0 | 11.2 | .012 | 3.658 | |
| I | 200 | 9.6 | 11.6 | .012 | 3.670 | |
| I | 200 | 10.0 | 11.2 | .012 | 3.682 | |
| 2 | 200 | 9.6 | 10.8 | .012 | 3.694 | |
| I | 200 | 9.2 | 10.8 | .012 | 3.706 | |
| 2 | 200 | 9.6 | 10.4 | .011 | 3.717 | |
| I | 200 | 9.2 | 10.8 | .012 | 3.729 | |
| I | 200 | 8.8 | 10.4 | .012 | 3.752 | |
| I | 200 | 9.2 | 10.8 | .012 | 3.752 | |
| I | 200 | 8.8 | 10.4 | .011 | 3.763 | |
| I | 200 | 8.8 | 10.4 | .012 | 3.775 | |
| I | 200 | 8.8 | 10.4 | .011 | 3.786 | |
| I | 200 | 9.2 | 10.8 | .012 | 3.798 | |
| I | 200 | 9.2 | 10.4 | .011 | 3.809 | |
| 2 | 200 | 8.4 | 10.0 | .011 | 3.820 | |
| I | 200 | 8.8 | 10.0 | .011 | 3.831 | |
| I | 200 | 8.8 | 10.4 | .011 | 3.842 | |
| 2 | 200 | 8.4 | 10.8 | .012 | 3.854 | |
| 2 | 200 | 8.4 | 10.0 | .011 | 3.865 | |
| I | 200 | 8.4 | 10.0 | .011 | 3.876 | |
| I | 200 | 8.4 | 9.6 | .011 | 3.887 | |
| 2 | 200 | 8.8 | 10.0 | .011 | 3.898 | |
| I | 200 | 8.4 | 10.0 | .011 | 3.909 | |

TABLE XI (Continued)

| Days standing | cc. of solution withdrawn | cc. of N/50 H ₂ SO ₄ to neutralize 100 cc. of the solution | | Estimated CaO Grams | Total CaO extracted Grams | Soluble Silica P.P.M. SiO ₂ |
|---------------|---------------------------|----------------------------------------------------------------------------------|---------------|---------------------|---------------------------|----------------------------------------|
| | | Phenolphthalein | Methyl Orange | | | |
| 3 | 200 | 8.8 | 9.6 | .011 | 3.920 | |
| 1 | 200 | 8.0 | 9.6 | .011 | 3.931 | |
| 1 | 200 | 8.4 | 10.0 | .011 | 3.942 | |
| 1 | 200 | 8.4 | 10.0 | .011 | 3.953 | |
| 3 | 200 | 8.0 | 9.6 | .011 | 3.964 | |
| 1 | 200 | 7.6 | 9.2 | .010 | 3.974 | |
| 1 | 200 | 8.0 | 9.6 | .011 | 3.985 | |
| 1 | 200 | 8.0 | 10.0 | .011 | 3.995 | |
| 3 | 200 | 8.0 | 9.6 | .011 | 4.007 | |
| 1 | 200 | 8.0 | 9.6 | .011 | 4.018 | |
| *1 | 200 | 8.0 | 9.6 | .011 | 4.029 | |
| 5 | 200 | 8.0 | 9.6 | .011 | 4.040 | |
| 1 | 200 | 7.2 | 8.8 | .010 | 4.050 | |
| 1 | 200 | 7.6 | 9.6 | .011 | 4.061 | |
| 1 | 200 | 8.0 | 9.6 | .011 | 4.072 | |
| 1 | 200 | 8.0 | 9.2 | .010 | 4.082 | |
| 2 | 200 | 7.6 | 9.2 | .010 | 4.092 | |
| 1 | 200 | 7.6 | 9.6 | .011 | 4.103 | |
| 1 | 200 | 8.0 | 9.2 | .010 | 4.113 | |
| 2 | 200 | 8.0 | 9.6 | .011 | 4.124 | |
| 1 | 200 | 8.0 | 9.2 | .010 | 4.134 | |
| 2 | 200 | 8.0 | 9.2 | .010 | 4.144 | |
| 1 | 200 | 7.2 | 9.2 | .010 | 4.154 | |
| 2 | 200 | 8.0 | 9.6 | .011 | 4.165 | |
| 1 | 200 | 7.6 | 9.6 | .011 | 4.176 | |
| 1 | 200 | 8.0 | 9.6 | .011 | 4.187 | |
| 2 | 200 | 7.6 | 9.6 | .011 | 4.198 | |
| 3 | 200 | 7.6 | 9.2 | .010 | 4.208 | |
| 1 | 200 | 7.2 | 9.2 | .010 | 4.218 | |
| 1 | 200 | 7.6 | 9.2 | .010 | 4.228 | |

*Approximately

The amount of CaO in the 150 cc. of solution remaining in the flask was approximately 0.146 gram. This is not taken into consideration in the extraction experiment, consequently the total CaO extracted as given in the table is also slightly in error. With the number of tests made it is readily seen that this error does not alter the fact that the results indicate adsorption of the calcium hydroxide by some compound of calcium and silica believed to be monocalcium silicate.

The CaO in Table XI is computed from the acid required to neutralize the solution when methyl orange is used for the indicator. One cc. of N/50 H_2SO_4 neutralizes approximately 0.00056 grams of CaO, and this factor was used in computing the CaO in the solution. When care is taken in making the titration tests the error should be very small.

A very striking proof of adsorption is when 0.45 gram of CaO was added at a certain stage of the extraction experiment, shown by Table XI and

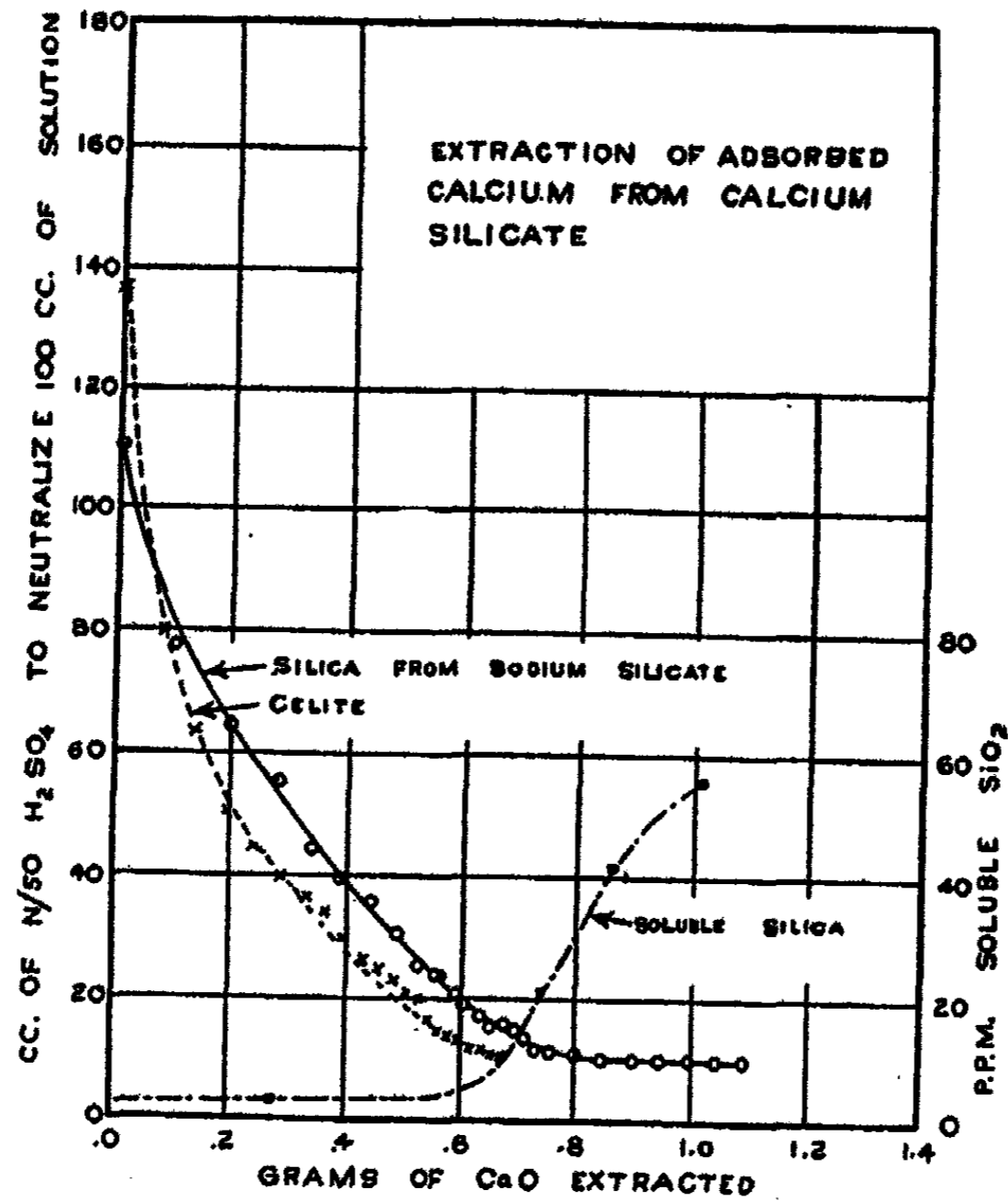


FIG. 4

the curve in Fig. 3. Extraction tests before the addition of this CaO are represented by circles on the curve and afterwards by x marks. It will be seen that when the amount of CaO added is subtracted from the total CaO extracted it gives a point almost exactly on the curve, then as the extraction test is continued the points coincide very closely. This indicates that the calcium hydroxide in solution and that which is assumed to be adsorbed give a reversible equilibrium as they should do if there is adsorption. In other words, when the $Ca(OH)_2$ in solution is increased more $Ca(OH)_2$ is adsorbed, and when decreased part of that which had been adsorbed is given off. There is not enough soluble silica when the alkali concentration re-

quires more than about 20 cc. of the N/50 acid to neutralize to be of any material consequence. This fact is of vital importance in supporting the assumption of adsorption.

Absolute equilibrium may not have been established within 24 hours, but in most cases a 10 cc. portion of the solution was tested shortly after the replacement with distilled water of the solution removed. These tests showed that equilibrium was nearly established within one hour. Table XI gives one instance in which the sample was held 24 days with practically no change in the alkalinity after the first few hours.

Extraction Experiment 2. In this experiment all the alkali in the sodium silicate was neutralized with hydrochloric acid and the precipitate washed practically free from chlorides.

The exact amount of silica used in this test was not determined, but it was much less than that in Experiment 1. The flask was filled to the 500 cc. mark and 250 cc. of the clear liquid were withdrawn at each test, making

TABLE XII
Extraction of adsorbed Calcium from Calcium Silicate

| Days standing | cc. of solution withdrawn | cc. of N/50 H ₂ SO ₄ to neutralize 100 cc. of the solution | | Estimated CaO Grams | Total CaO extracted Grams | Soluble Silica P.P.M. (SiO ₂) |
|---------------|---------------------------|----------------------------------------------------------------------------------|---------------|---------------------|---------------------------|-------------------------------------------|
| | | Phenolphthalein | Methyl Orange | | | |
| 2 | 0 | 105.0 | 110.0 | | | |
| 1 | 250 | 76.0 | 78.0 | .109 | .109 | |
| 1 | 250 | 62.0 | 64.0 | .090 | .199 | |
| 1 | | 52.0 | 54.0 | | | |
| 3 | 250 | 53.0 | 55.0 | .077 | .276 | 3.0 |
| 1 | 250 | 42.0 | 44.0 | .062 | .338 | |
| 1 | 250 | 37.0 | 39.0 | .055 | .393 | |
| 1 | 250 | 33.2 | 35.2 | .049 | .442 | |
| 1 | 250 | 28.8 | 30.0 | .042 | .484 | |
| 1 | 250 | 24.4 | 25.6 | .036 | .520 | |
| 1 | | 21.0 | 23.0 | | | |
| 2 | | 22.0 | 24.0 | | | |
| 3 | | 22.0 | 24.0 | | | |
| 5 | 250 | 23.0 | 24.0 | .034 | .554 | |
| 1 | 250 | 19.5 | 20.5 | .029 | .583 | |
| 1 | 250 | 16.0 | 18.0 | .025 | .608 | |
| 2 | | 16.0 | 17.2 | | | |
| 4 | 250 | 16.0 | 17.2 | .024 | .632 | |
| 1 | 250 | 14.0 | 15.0 | .021 | .653 | |
| 4 | 250 | 14.4 | 15.6 | .022 | .675 | |

TABLE XII (Continued)

| Days standing | cc. of solution withdrawn | cc. of N/50 H ₂ SO ₄ to neutralize 100 cc. of the solution | | Estimated CaO Grams | Total CaO extracted Grams | Soluble Silica P.P.M. (SiO ₂) |
|---------------|---------------------------|----------------------------------------------------------------------------------|---------------|---------------------|---------------------------|-------------------------------------------|
| | | Phenolphthalein | Methyl Orange | | | |
| 2 | | 12.8 | 14.4 | | | |
| 30 | 250 | 12.6 | 14.2 | .020 | .695 | |
| 2 | 250 | 11.2 | 12.8 | .018 | .713 | |
| 1 | 250 | 10.0 | 11.2 | .016 | .729 | 21.0 |
| 1 | 250 | 9.6 | 11.2 | .016 | .745 | |
| 1 | 250 | 9.2 | 11.0 | .015 | .760 | |
| 1 | 250 | 9.4 | 11.0 | .015 | .775 | |
| 1 | 250 | 8.8 | 10.4 | .015 | .790 | |
| 1 | 250 | 8.4 | 10.2 | .014 | .804 | |
| 1 | 250 | 8.0 | 10.0 | .014 | .818 | |
| 1 | | 7.6 | 9.2 | | | |
| 2 | | 8.0 | 9.6 | | | |
| 3 | 250 | 8.0 | 9.6 | .013 | .831 | |
| 1 | 250 | 7.2 | 8.6 | .012 | .843 | |
| 1 | 250 | 7.2 | 8.6 | .012 | .855 | |
| 1 | 250 | 7.2 | 8.6 | .012 | .867 | |
| 1 | 250 | 7.2 | 8.6 | .012 | .879 | 40.7 |
| 1 | 250 | 7.2 | 9.2 | .013 | .892 | |
| 1 | 250 | 7.2 | 8.6 | .012 | .904 | |
| 1 | 250 | 7.2 | 8.6 | .012 | .916 | |
| 1 | 250 | 7.2 | 8.6 | .012 | .928 | |
| 1 | 250 | 7.2 | 8.8 | .012 | .940 | |
| 1 | 250 | 7.2 | 8.8 | .012 | .952 | |
| 1 | 250 | 7.4 | 8.8 | .012 | .964 | |
| 1 | 250 | 7.4 | 9.0 | .012 | .976 | |
| 1 | 250 | 7.4 | 9.0 | .012 | .988 | |
| 1 | 250 | 7.2 | 8.8 | .012 | 1.000 | |
| 1 | 250 | 7.2 | 8.8 | .012 | 1.012 | |
| 1 | 250 | 6.8 | 8.4 | .012 | 1.024 | 55.0 |
| 1 | 250 | 6.8 | 8.0 | .011 | 1.035 | |
| 1 | 250 | 7.2 | 8.6 | .012 | 1.047 | |
| 1 | 250 | 6.8 | 8.4 | .012 | 1.059 | |
| 1 | 250 | 7.2 | 8.6 | .012 | 1.071 | |
| 1 | 250 | 6.4 | 7.2 | .010 | 1.081 | |
| 1 | 250 | 6.8 | 8.4 | .012 | 1.093 | |

the dilution when refilled 50 percent. The alkali concentration of the solution after the addition of 2.5 grams of CaO, all at one time, and standing 2 days with frequent agitation required 110 cc. of the N/50 acid per 100 cc. of the solution to neutralize. This is approximately one-half the saturation point of calcium hydroxide at room temperature. There was no sodium in the solution in this experiment as was the case for Experiment 1. Table XII gives the alkali concentration of the solution as the calcium was extracted. This is also shown by the solid line in Fig. 4.

TABLE XIII

Extraction of adsorbed Calcium from Calcium Silicate produced by adding Lime to "Celite"

| Days standing | cc. of solution withdrawn | cc. of N/50 H ₂ SO ₄ to neutralize 100 cc. of the solution | | Estimated CaO Grams | Total CaO extracted Grams |
|---------------|---------------------------|----------------------------------------------------------------------------------|---------------|---------------------|---------------------------|
| | | Phenolphthalein | Methyl Orange | | |
| 25 | 0 | 134.0 | 137.0 | | |
| 11 | 180 | 77.0 | 80.0 | .081 | .081 |
| 6 | 166 | 61.0 | 63.0 | .059 | .140 |
| 6 | 200 | 48.0 | 50.0 | .056 | .196 |
| 2 | 200 | 42.0 | 44.0 | .049 | .245 |
| 2 | 200 | 37.9 | 39.5 | .044 | .289 |
| 2 | 200 | 34.4 | 36.4 | .041 | .330 |
| 3 | 200 | 31.2 | 32.8 | .037 | .367 |
| 3 | 200 | 27.6 | 28.8 | .032 | .399 |
| 3 | 200 | 24.4 | 26.4 | .029 | .428 |
| 3 | 200 | 23.0 | 24.4 | .027 | .455 |
| 3 | 200 | 21.2 | 23.2 | .026 | .481 |
| 2 | 200 | 19.2 | 20.2 | .023 | .504 |
| 2 | 200 | 18.0 | 19.6 | .022 | .525 |
| 1 | 200 | 15.2 | 16.0 | .011 | .544 |
| 1 | 200 | 13.6 | 14.4 | .016 | .560 |
| 1 | 200 | 12.6 | 13.4 | .015 | .575 |
| 1 | 200 | 11.6 | 13.2 | .015 | .590 |
| 1 | 200 | 11.2 | 12.4 | .014 | .604 |
| 1 | 200 | 10.4 | 11.6 | .013 | .617 |
| 1 | 200 | 9.6 | 11.0 | .012 | .629 |
| 1 | 200 | 10.0 | 11.2 | .012 | .641 |
| 1 | 200 | 9.2 | 10.4 | .011 | .652 |
| 1 | 200 | 8.8 | 10.0 | .011 | .663 |
| 1 | 200 | 8.4 | 9.6 | .010 | .673 |

When the table shows no solution removed, only 10 to 25 cc. were removed for testing and the sample was held over for a longer period without the addition of more distilled water. In one instance the sample was held 30 days with practically no change in the alkali concentration of the solution over what it was at 24 hours.

Extraction Experiment 3. In this experiment 3.0 grams of commercial lime testing 92 percent water soluble CaO was added to 3.4 grams of "Celite." This is a trade name for a diatomaceous earth frequently used in small quantities in concrete. The dry "Celite" was placed in a 300 cc. Pyrex flask and the flask filled to the 300 cc. mark with distilled water. The lime was added in small weighed quantities over a period of 32 days; then it was allowed to stand 25 days before the extraction test was started. One cc. of N/50 NaOH was also added. The reaction of the lime with the "Celite" was very much slower than for the experiments using a gelatinous hydrous oxide of silica. The extraction tests given in Table XIII and shown by the broken line in Fig. 4 show it to have the same characteristics as the other silica.

"Celite" probably is not pure silica, and all the silica present may not be in a form that readily unites with calcium hydroxide. The test, however, gives evidence of adsorption the same as the tests where the pure silica jelly is used. There was approximately the same amount of calcium oxide used in both Extraction Experiments 2 and 3. It is also noted that the two curves in Fig. 4 coincide very closely.

All Experiments Indicate Adsorption of Calcium Hydroxide by Calcium Silicate

The significant fact brought out by these experiments is that silica of certain forms when in contact with a solution of calcium hydroxide will establish equilibrium at any point between the equilibrium of some compound believed to be monocalcium silicate and the saturation point of calcium hydroxide in water, depending on the amount of calcium hydroxide in solution. This equilibrium is approximately the same whether established by the addition of calcium hydroxide or by the extraction of calcium hydroxide. Compounds of calcium and silica of a higher calcium content than CaO, SiO_2 are thought by many to undergo hydrolysis to the extent of producing calcium hydroxide crystals. This may be the case, but the compound of lower calcium content evidently adsorbs calcium hydroxide until some condition of surface equilibrium is established. How much calcium can be adsorbed is not known definitely, but the experiments indicate that 30 to 45 percent as much calcium can be adsorbed as is present as CaO, SiO_2 .

It is believed that the power of adsorption has great influence in retarding the hydrolysis or breaking down of the high calcium compounds in hydrated portland cement which is submerged in water. The writer conducted extraction tests on concrete which had been exposed to water over 10 years, and these tests also gave evidence of adsorption of calcium hydroxide by calcium silicate, or some compound in the concrete. The reversible equilib-

rium due to increasing the calcium hydroxide concentration of the solution was not so pronounced, however, as with pure silica jelly. This may be due to the silica uniting with the alumina, as the calcium is extracted, to form an aluminum silicate, which compound may not adsorb calcium hydroxide to any material extent.

Lerch and Bogue¹ attribute the varying pH or alkali concentration in the hydrolysis of the calcium silicates likely to be found in portland cement to dissociation of these compounds, and give possible equations for the stages of hydrolysis from $3\text{CaO},\text{SiO}_2$ to CaO,SiO_2 . It is difficult to understand how they arrive at such a conclusion, for there is no evidence in their paper or in any previous work on the calcium silicates so far as the writer could find to support such an assumption.

In the discussion of a paper by the writer, Bogue² takes exception to the statement that there is evidence of adsorption by the cement compounds, and states:

"The curves presented are typical curves for hydrolysis. Any salt which contains either a weak acid radical, or a weak basic radical, or both, will undergo in water a decomposition into its acidic and basic constituents. . . . Thus, in the data presented by the author, there is nothing that is not altogether comprehensible and completely explainable on the basis of the recognized laws and theories of chemistry. The injection of a theory of surface adsorption seems unnecessary and unwarranted."

Certainly no one believes that 2 to 6 parts per million of SiO_2 , even if it all existed in the dissociated state, can materially affect the pH or alkali concentration of a solution containing from 200 to 1,000 parts per million of calcium hydroxide. To explain the large amount of calcium hydroxide going into some kind of a combination with the silica over that necessary to form CaO,SiO_2 , it must be assumed that a definite compound of higher calcium content is formed or that there is adsorption. While it may be possible for some other compound to be formed, the evidence does not seem to justify such an assumption. Bogue cannot be correct unless he is assuming that the surface molecules of the solid calcium silicate are dissociated and can attract the calcium ions, which after all is nothing but adsorption. This, however, is not saying that the surface molecules or ions of certain solids are dissociated, but that they have the power of uniting with or drawing to the surface ions of a different electric charge.

Summary

Reactions of calcium oxide and silica are of great importance; e.g. in the building industry.

There appears to be a compound of calcium oxide and silica approximately equal to the hydrated CaO,SiO_2 formed when calcium oxide is added to a

¹ Lerch and Bogue: *J. Phys. Chem.*, 31, 1627 (1927).

² *Corrosion of Concrete*. Discussion by R. H. Bogue: *Proc. Am. Soc. Civil Engineers*, 52, 1270 (1926).

solution containing silica in a solid form such as the hydrous oxide of silica.

The addition of more calcium oxide to the solution will establish equilibria between the solid and the calcium hydroxide in solution that vary from the solubility equilibrium of monocalcium silicate to approximately the saturation point of calcium hydroxide. Calcium hydroxide to the extent of approximately 30 to 45 per cent of the calcium hydroxide united with the silica appears to be adsorbed by the monocalcium silicate, or whatever be the definite compound of calcium and silica.

The equilibrium between the monocalcium silicate and its adsorbed calcium, and the calcium hydroxide in solution is reversible. By increasing or reducing the calcium hydroxide in solution calcium is adsorbed or released by the silicate.

The assumption that dissociation of the calcium silicates causes the variable pH or alkali concentration as the calcium is leached out is not correct.

It is possible that the condition of surface equilibrium due to adsorption materially retards the rate of hydrolysis of some of the compounds in concrete which is submerged in water.

The writer wishes to acknowledge several valuable suggestions made by Mr. Frank Hannan in the interpretation of the data and in the arrangement of the manuscript.

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OXIDATION OF CARBOHYDRATES, FATS, AND NITROGENOUS PRODUCTS BY AIR IN PRESENCE OF SUNLIGHT

BY C. C. PALIT AND N. R. DHAR

In foregoing publications¹ we have shown that different carbohydrates, nitrogenous products, alcohols, etc. which are not ordinarily oxidised by air, are readily oxidised by air in presence of reducing agents like sodium sulphite, ferrous hydroxide, cerous hydroxide, manganous hydroxide and other reducing agents.

In a recent communication² we have shown that methyl alcohol, ethyl alcohol, and glycerol can be oxidised by passing air at the ordinary temperature in presence of sunlight. Moreover several years ago, one of us³ pointed out that reactions which are sensitive to the influence of light are also induced to take place in presence of another chemical change of the same type.

In this paper, we are recording the experimental results obtained in the oxidation of several carbohydrates, urea, glycine, hippuric acid, potassium stearate, palmitate and oleate by passing air through these solutions in presence of tropical sunlight. Glass bottles containing solutions of various substances were exposed to sunlight and a definite volume of air was passed through them; and the amounts of unoxidised substances were estimated after passing 36.5 litres of air in 5½ hours.

In these experiments, a slow current of air was passed through a series of bottles containing solutions of carbohydrates, nitrogenous substances and fats respectively. In each case 10 cc. of the solutions under investigation were taken and the volume was made up to 100 cc. In the case of carbohydrates and glycogen, these were estimated after hydrolysis when necessary by reduction of Fehling's solution. The cuprous oxide obtained was collected, dried, and ignited in a crucible and weighed as cupric oxide. In case of nitrogenous substances, urea was estimated by freshly prepared alkaline solution of sodium hypobromite in an ureometer. After introduction of a known volume of solution of urea, the whole system was set apart over night and the readings noted on the following day. By this method, an accurate result was obtained and the necessary correction was not needed at all. Uric acid was determined by treating the solution with concentrated H₂SO₄ and then titrating against standard potassium permanganate solution whilst the solution was hot.

The amino-acids, viz. glycine, alanine, and hippuric acid, were estimated by adding 10 cc. of neutralised solution of formaldehyde (1 part formaldehyde diluted with 2 parts of water) and titrating the mixture with N/10 sodium hydroxide solution using phenolphthalein as indicator. This method

¹ J. Phys. Chem., 29, 376 (1925); 30, 939 (1926).

² J. Phys. Chem., 29, 926 (1925).

³ J. Chem. Soc., 111, 694 (1917).

of determination gives accurate results. The fats viz. potassium stearate, potassium oleate and potassium palmitate were treated with 10 cc. of iodine trichloride and kept for 2 hours in the dark; and then the whole solution was treated with N/10 sodium thiosulphate solution by adding potassium iodide solution.

The following experimental results were obtained.

TABLE I (A)

In each of these experiments, the volume of air passed was 36.5 litres in $5\frac{1}{2}$ hours

| No. of Experiment | Substance used in the experiment | Actual weight of substance in 10 cc. of the solution taken in gm. (Blank) | Amount of substance oxidised in gm. | Percentage amount of substance oxidised |
|-------------------|----------------------------------|---------------------------------------------------------------------------|-------------------------------------|-----------------------------------------|
| 1 | Galactose | 0.0861 | 0.0059 | 6.8 |
| 2 | Arabinose | 0.1000 | 0.0060 | 6.0 |
| 3 | Cane sugar | 0.0964 | 0.0071 | 7.4 |
| 4 | Glucose | 0.0962 | 0.0076 | 7.9 |
| 5 | Laevulose | 0.09185 | 0.0079 | 8.6 |
| 6 | Lactose | 0.0997 | 0.0142 | 16.2 |
| 7 | Maltose | 0.1097 | 0.0220 | 20.0 |
| 8 | Starch | 0.1027 | 0.0366 | 35.6 |
| 9 | Glycogen | 0.0987 | 0.0157 | 15.9 |

TABLE I (B)

In each of these experiments, the volume of air passed was 36.5 litres in $5\frac{1}{2}$ hours

| No. of Experiment | Substance used in the experiment | Actual weight of substance in 10 cc. of the solution taken in gm. (Blank) | Amount of substance oxidised in gm. | Percentage amount of substance oxidised |
|-------------------|----------------------------------|---------------------------------------------------------------------------|-------------------------------------|-----------------------------------------|
| 1 | Arabinose | 0.1000 | 0.0075 | 7.5 |
| 2 | Galactose | 0.0861 | 0.0067 | 7.8 |
| 3 | Cane sugar | 0.0964 | 0.0098 | 10.2 |
| 4 | Glucose | 0.0962 | 0.0144 | 14.9 |
| 5 | Laevulose | 0.09185 | 0.0159 | 17.3 |
| 6 | Lactose | 0.0977 | 0.0197 | 19.7 |
| 7 | Maltose | 0.1097 | 0.0285 | 25.9 |
| 8 | Starch | 0.1027 | 0.0399 | 38.8 |
| 9 | Glycogen | 0.0987 | 0.0987 | 19.7 |

N. B. In these experiments, the intensity of light was greater than that in previous experiments shown in Table I (A).

The results prove conclusively that solutions of cane sugar, glucose, galactose, maltose, laevulose, lactose, arabinose, starch, and glycogen can be oxidised by passing air through these solutions in presence of sunlight.

The amounts of oxidation of the various carbohydrates are in the following decreasing order:— Starch > maltose > lactose > laevulose > glucose > cane sugar > galactose > arabinose.

We have repeatedly observed that the amount of oxidation varies as the intensity of light [Vide Table I (B)].

Having obtained the results to show that oxidation of the carbohydrates does take place in presence of sunlight, we carried on experiments with certain nitrogenous substances and the results given in Table II were obtained.

TABLE II

In each of these experiments, the volume of air passed was 36.5 litres in 5½ hours

| No. of Experiment | Substance used in the experiment | Actual weight of substance in 10 cc. of the solution taken in grm. (Blank) | Amount of substance oxidised in grm. | Percentage amount of substance oxidised |
|-------------------|----------------------------------|----------------------------------------------------------------------------|--------------------------------------|-----------------------------------------|
| 1 | Urea | 0.2000 | 0.0175 | 8.7 |
| 2 | Glycine | 0.0999 | 0.0096 | 9.6 |
| 3 | α -Alanine | 0.0997 | 0.0365 | 36.6 |
| 4 | Hippuric acid | 0.0483 | 0.0069 | 14.2 |
| 5 | Sodium urate | 0.0420 | 0.00825 | 19.6 |

The foregoing results prove that solutions of urea, uric acid, hippuric acid, glycine, alanine, etc., can be oxidised in presence of sunlight by passing air.

Next we have investigated the oxidation of potassium stearate, potassium palmitate, and potassium oleate and have obtained the results given in Table III.

TABLE III

Experiments with fats. The volume of air passed was 36.5 litres in 5½ hours. 10 cc. of iodine trichloride + 10 cc. of 10% potassium iodide solution \equiv 16.0 cc. of N/10 sodium thiosulphate

| No. of Experiment | Substance used in the experiment | Volume in cc. of N/10 sodium thio-sulphate required for 10 cc. of fat taken. (Blank) | Volume in cc. of N/10 sodium thio-sulphate required for fat left after the experiment | Percentage amount of fat oxidised |
|-------------------|----------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|-----------------------------------|
| 1 | Potassium stearate | 15.25 | 15.55 | 40 |
| 2 | Potassium oleate | 10.45 | 12.2 | 31.5 |
| 3 | Potassium palmitate | 13.55 | 14.45 | 36.7 |

Hence these fatty substances are also oxidised by passing air in presence of sunlight.

The foregoing experimental results show that carbohydrates, nitrogenous matters and fatty substances have been oxidised for the first time simply by passing air in presence of sunlight; and these results are likely to throw considerable light on understanding the use of sunlight and artificial lights in the treatment of several diseases.

We have also tried to oxidise solutions of sodium nitrite, sodium arsenite, arsenious acid, and potassium oxalate in presence of sunlight by passing air. No oxidation was observed with sodium nitrite, sodium arsenite and arsenious acid. The results obtained with $K_2C_2O_4$ are given in Table IV.

TABLE IV

Experiment with potassium oxalate. In this experiment, the volume of air passed was 36.5 litres in $5\frac{1}{2}$ hours.

10 cc. of potassium oxalate \equiv 15.4 cc. of N/10 $KMnO_4$

| No. of Experiment | Substance used in the experiment | Volume in cc. of N/10 $KMnO_4$ required for 10 cc. of potassium oxalate (Blank) | Volumes in cc. of N/10 $KMnO_4$ required for the oxalate left after the experiment | Amount of oxalate oxidised in terms of volume in cc. of N/10 $KMnO_4$ | Percentage amount of oxalate oxidised |
|-------------------|----------------------------------|---------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-----------------------------------------------------------------------|---------------------------------------|
| 1 | Potassium oxalate | 15.4 | 13.05 | 2.35 | 15.2 |
| 2 | Potassium oxalate | 15.4 | 10.8* | 4.6* | 29.8* |

* In this experiment, the intensity of light used was much greater than that used in the first experiment, thus showing greater amount of oxidation with increase in the intensity of light.

It is well-known that oxalate ion, $C_2O_4^{2-}$, is photosensitive and we have proved that it can be oxidised by passing air in presence of sunlight.

TABLE V (A)

In each of these experiments, the volume of air passed was 36.5 litres in $5\frac{1}{2}$ hours. The weight of zinc oxide taken was exactly 0.5 grms.

| No. of Experiment | Substance used in the experiment | Actual weight of substance in 10 cc. of the solution taken in gm. (Blank) | Amount of substance oxidised in gm. | Percentage amount of substance oxidised |
|-------------------|----------------------------------|---------------------------------------------------------------------------|-------------------------------------|-----------------------------------------|
| 1 | Arabinose | 0.10000 | 0.0110 | 11.0 |
| 2 | Galactose | 0.0861 | 0.0101 | 11.7 |
| 3 | Glucose | 0.0962 | 0.0114 | 11.8 |
| 4 | Laevulose | 0.09185 | 0.0117 | 12.7 |
| 5 | Cane sugar | 0.0969 | 0.0128 | 13.2 |
| 6 | Lactose | 0.0997 | 0.0402 | 41.9 |
| 7 | Maltose | 0.1097 | 0.0454 | 41.3 |
| 8 | Starch | 0.1027 | 0.0688 | 66.9 |
| 9 | Glycogen | 0.0987 | 0.0382 | 38.7 |
| 10 | Glycine | 0.0999 | 0.0452 | 45.2 |
| 11 | α -Alanine | 0.0997 | 0.0481 | 48.2 |
| 12 | Hippuric acid | 0.0492 | 0.0206 | 41.8 |
| 13 | Sodium urate | 0.1575 | 0.0037 | 22.5 |
| 14 | Urea | 0.2000 | 0.0200 | 10.0 |

In a recent paper we have proved that zinc oxide is a powerful photochemical sensitiser and many photochemical reactions have been accelerated by the presence of zinc oxide. We have carried on experiments on the oxidation of carbohydrates, glycogen, nitrogenous substances, and fats in sunlight in presence of zinc oxide. The results obtained are given in Table V.

TABLE V (B)

Experiments with fats. Weight of zinc oxide taken was 0.5 grms. 10 cc. of ICl_3 + 10 cc. of 10% KI \equiv 16.0 cc. of N/10 sodium thiosulphate

| No. of Experiment | Substance used in the experiment | Volume in cc. of N/10 sodium thiosulphate required for 10 cc. of fat taken. (Blank) | Volume in cc. of N/10 sodium thiosulphate required for the fat left after the experiment | Percentage amount of fat oxidised |
|-------------------|----------------------------------|-------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|-----------------------------------|
| 1 | Potassium stearate | 15.25 | 15.60 | 46.6 |
| 2 | Potassium oleate | 10.45 | 12.4 | 35.1 |
| 3 | Potassium palmitate | 13.55 | 14.55 | 40.8 |

TABLE V (C)

Experiment with potassium oxalate. $\text{ZnO} = 0.5$ gm. 10 cc. of potassium oxalate \equiv 10.8 cc. of N/10 KMnO_4

| No. of Experiment | Substance used in the experiment | Volume in cc. of N/10 KMnO_4 required for 10 cc. of potassium oxalate solution taken (Blank) | Volume in cc. of N/10 KMnO_4 required for oxalate left after the experiment | Amount of oxalate oxidised in terms of volume in cc. of N/10 KMnO_4 | Percentage amount of oxalate oxidised |
|-------------------|----------------------------------|-------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|------------------------------------------------------------------------------|---------------------------------------|
| 1 | Potassium oxalate | 10.8 | 7.3 | 3.5 | 32.4 |

The foregoing experimental results show that the amount of oxidation is greater in presence of zinc oxide, which acts as a photosensitiser.

Sunlight and artificial lights have been used with great success in the treatment of tuberculosis, pernicious anaemia, rickets, etc. In some previous publications¹ we have emphasised the importance of sunlight in the treatment of deficiency diseases and we have observed that rickets, osteomalacia, beri-beri, pellagra, etc. would have been more common in poor tropical countries like India and China, had not the compensating agent, sunlight, been present.

This conclusion has been corroborated by some experiments carried on in these laboratories. Two lots of pigeons were fed on polished rice for about six months. One lot had plenty of sunlight whilst the other had very little of it. The lot which had sunshine did not show any signs of polyneuritis whilst the other lot not having sunshine had stomachic troubles first and then showed definite signs of polyneuritis.

¹ Dhar: *Chemie der Zelle und Gewebe*, 12, 217, 225, 317 (1925); 13, 209 (1926).

We are of the opinion that in the presence of sunlight the metabolism of the food materials taken in the system is accelerated and that is how disease is avoided. We believe that by absorption of sunlight the body cells are activated and greater amounts of oxidation of carbohydrates, fats and proteins take place than in the absence of sunlight. It seems pretty generally accepted that several diseases are caused by defective metabolism. We are of opinion that in these diseases, which are caused by the want of proper metabolism, sunlight or artificial light should be highly efficacious, because as we have proved experimentally the oxidation of fats, carbohydrates and nitrogenous matter is greatly accelerated by light.

Summary and Conclusion

1. Solutions of galactose, arabinose, cane sugar, glucose, laevulose, lactose, maltose, starch, glycogen, urea, glycine, α -alanine, hippuric acid, sodium urate, potassium stearate, potassium oleate, potassium palmitate, and potassium oxalate have been oxidised by passing air in presence of sunlight.
2. It has been found that the greater the intensity of sunlight, the greater is the amount of oxidation.
3. Zinc oxide acts as a powerful photo-sensitiser in the above oxidations and in its presence the amount of oxidation in each case is greater than in its absence.
4. It is probable that by the absorption of sunlight, the cells in the animal body are activated and this activation leads to a greater amount of oxidation of fats, carbohydrates and proteins. Hence sunlight and other kinds of artificial lights prove efficacious in the treatment of diseases specially of metabolic origin.

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June, 1927*

THE INFLUENCE OF LIGHT ON THE COLOR OF FERRIC CHLORIDE SOLUTIONS

BY KENNETH S. RITCHIE

Several years ago, in connection with the development of a spectro-colorimeter, ferric chloride solutions were used for the production of standard colors. A stock solution of ferric chloride was first prepared by dissolving clean iron wire (Baker's "Iron Wire for Standardizing—99.84% Fe") in aqua regia, the excess nitric acid being subsequently destroyed by three evaporations with concentrated hydrochloric acid. The residue was then treated with excess dilute hydrochloric acid and brought to a concentration of approximately 200 gm. of dissolved iron per liter. In preparing this stock solution, C. P. acid was always employed. This stock solution, containing ferric chloride and excess hydrochloric acid, was kept in a bottle wrapped with black glazed paper and from time to time other ferric chloride solutions were prepared from it by suitable dilution. Under these conditions color tints of constant values were obtained and used as standards for colorimetric work over a period of two years.

However, upon exposure to strong sunlight or to strong artificial light, color changes took place in the ferric chloride solutions. The direction of these changes was reversed as soon as the solutions were withdrawn from the influence of the light and in certain instances measurements showed that the original color had returned. As a search of the literature failed to reveal any record of similar observations by other investigators working with ferric chloride solutions, a preliminary study was undertaken to learn more about the effect of light on the color of these solutions.

Some semi-quantitative experiments involving the effect of strong sunlight upon the stock solution and various dilutions thereof were first made. These showed an increase in the color intensity of about 15% after one day's exposure and somewhat smaller effects for succeeding days. These measurements were made with a Kober-Klett colorimeter but without temperature regulation during the exposure period. The original color intensity returned after the ferric chloride solutions had remained in the subdued light of the laboratory for several days.

Later the development of the spectro-colorimeter¹ afforded an opportunity to study the light sensitivity of the ferric chloride solutions in more detail and particularly to determine the spectral curves which show the changes occurring in different regions of the spectrum. In one experiment, for instance, the stock solution diluted to one-fourth of its original concentration was employed. This liquid was exposed to the influence of the intense light from the lamp in the spectro-colorimeter, while a stream of air carried the

¹ A paper describing this instrument will probably be published during the coming year.

heat resulting from the absorption of radiation away from the solution cup and thereby kept the temperature of the liquid practically constant. Under these conditions four sets of measurements were made after light exposures of $\frac{1}{2}$, $1\frac{1}{2}$, 5 and $6\frac{1}{2}$ hours, respectively. The results obtained are shown graphically in Fig. 1, in which the fraction of the incident light transmitted by the solution is plotted as ordinate against the (decreasing) wave length of the

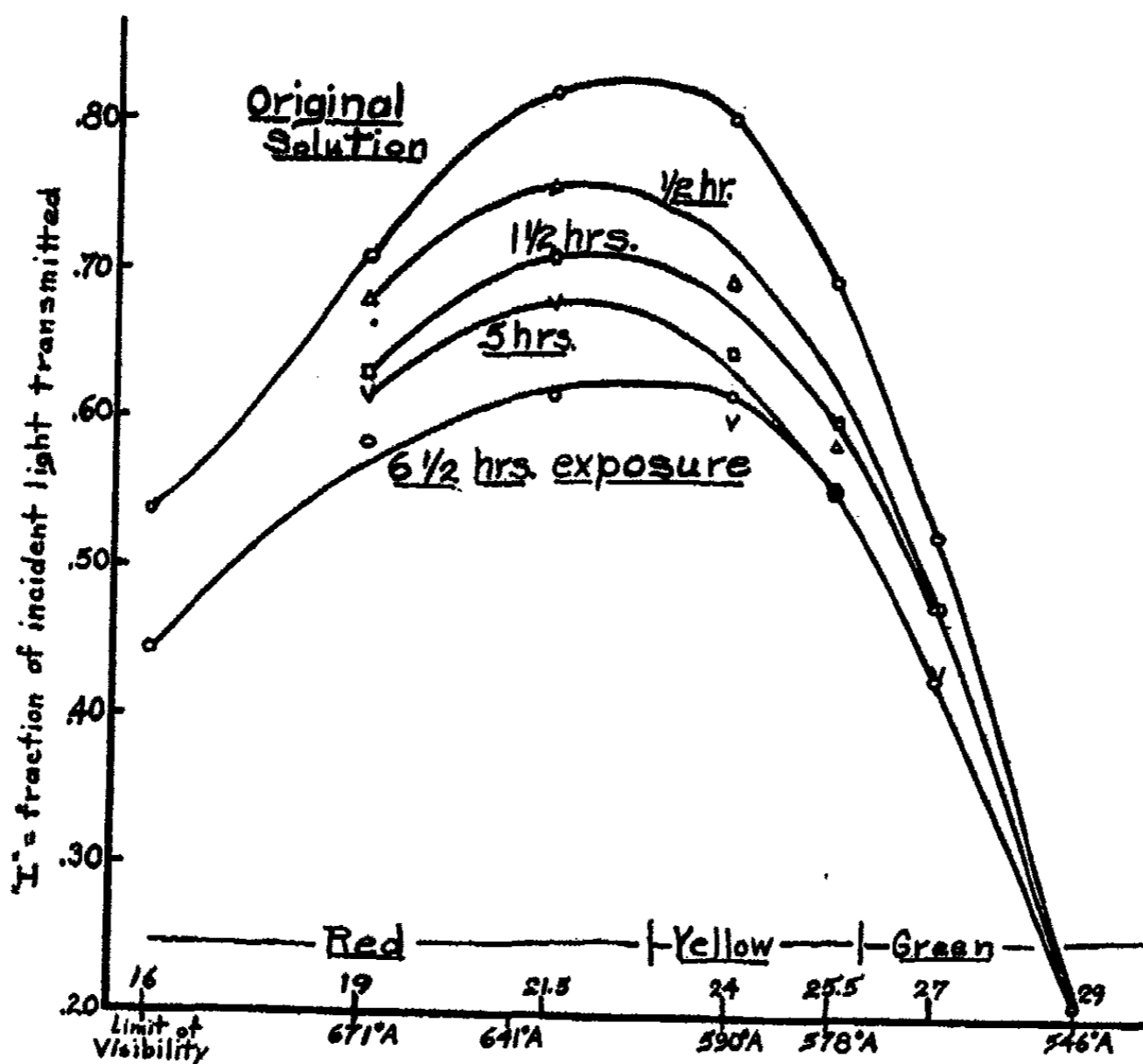


FIG. 1

light as abscissa. It is evident that there is a marked increase in the light absorption in various parts of the spectrum and that on the whole the effect of equal times of exposure becomes progressively less with increasing time.

From these experiments, it is evident that exposure to intense light produces a photochemical change in the three-component system H_2O , HCl , $FeCl_3$. This change is, moreover, reversible and the solutions slowly return to their initial condition on removal of the light. A change, somewhat similar to this produced by radiation, was also observed when the ferric chloride solutions were heated to $85^\circ C$ for a half-hour period. The resulting liquid, when cooled to room temperature, then gave an increased light absorption comparable to that obtained by $1\frac{1}{2}$ hour's exposure to light. In this latter

case, the effect of heating is possibly to partially hydrolyze the ferric chloride in solution; and, hence, the intense radiation may be doing the same at a much lower temperature.

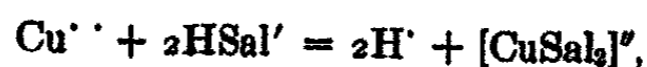
While the present study is only preliminary, it has seemed best to publish the results thus obtained, as a continuation of the investigation in the immediate future is improbable and a search of the literature has failed to show any record of similar observations on the sensitivity of the color of ferric chloride solutions to light. Before concluding the author wishes to thank Professor S. W. Young for his kindly guidance in the research and Professor George S. Parks for advice in preparing the manuscript.

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THE TRANSPORT NUMBER OF THE CATION IN AQUEOUS SOLUTIONS OF NICKEL SALICYLATE

BY FREDERICK ELSTON JONES AND C. R. BURY

In a previous communication from this laboratory¹ it was suggested that copper salicylate ionised in aqueous solution either as a normal cupric salt or as a complex cupri-salicylic acid²:—



(where H_2Sal = salicylic acid), the mode of ionisation depending primarily on the hydrogen ion concentration. So far as could be detected from transport number determinations, the first method of ionisation (as a cupric salt) alone occurred in neutral solutions, though the existence of traces of complex acid have since been detected by hydrogen ion determinations³. As a result of the formation of undissociated salicylic acid it was shown that the ratio $[\text{CuSal}_2]'/\text{Cu}^{++}$ should increase with concentration: this could not be demonstrated experimentally owing to the low solubility of copper salicylate. It therefore seemed of interest to determine the transport numbers of nickel salicylate, which is much more soluble than, but in other respects similar to copper salicylate.

Experimental

Nickel salicylate was prepared by dissolving freshly precipitated nickel hydroxide in excess salicylic acid suspended in water at about 60°C. The resulting solution was concentrated by evaporation, the temperature being kept below 60°, then cooled and filtered: the tetrahydrate crystallised out on inoculation. This was washed with aqueous alcohol to remove the last traces of acid and recrystallised from water.

Its solubility was found to be 70.04 grams (0.2105 mols) per 1000 grams of water at 25°C. It is therefore about seven times as soluble as the corresponding copper compound. Nickel was determined quantitatively, in the solubility determination and in the transport number experiments, by the potassium cyanide volumetric method.⁴

Transport numbers were determined by the same procedure as was used with copper salicylate, except that a smaller cell of 80 cc. capacity was used for the more concentrated solutions, and silver coulometers of the Rayleigh type, as described by Rosa and Vinal⁵, were employed.

¹ J. Chem. Soc., 131, 333 (1927).

² It is not improbable that the monobasic acid $\text{H}[\text{HSalCuSal}]$ exists as an intermediate stage in this transformation, in which case the equilibrium constant deduced for the reaction is not valid.

³ Wark: J. Chem. Soc., 131, 1753 (1927).

⁴ Sutton: "Volumetric Analysis", 270 (1900).

⁵ Bull. Bureau Standards, 9, 172 (1913).

As with the copper salt, a gelatinous precipitate is formed at the cathode, and transport numbers are therefore based on analysis of the anode portions only. During electrolysis, one gram molecule of salicylic acid per faraday is liberated at the anode: some of this remains in solution while some crystallises out. In order to obtain consistent and accurate results, it was found necessary to transfer the acid completely with the anode portion from the cell, by washing out the latter with small amounts of the original solution, and to deduct its weight, calculated from the coulometer reading, from the weight of the anode portion.

For example, in one experiment the original solution contained 0.002911 gm. Ni per gram of water (or 0.04960 mols per 1000 gm.), while the anode portion, weighing 71.687 gm., was found to contain 0.1623 gm. Ni (= 0.9204 gm. Ni(SalH)₂). The mean weight of silver deposited in the coulometers was 0.25675 gm., which corresponds to a loss of 0.06983 gm. Ni from the cell, and to the liberation of 0.329 gm. H₂Sal at the anode. The weight of water in the anode portion was therefore 71.687 - 0.920 - 0.329 = 70.438 gm. The loss of nickel from the anode portion was therefore 70.438 × 0.002911 - 0.1623 = 0.04274 gm., and the transport number 0.04274 ÷ 0.06983 = 0.612. In dilute solutions the weight of salicylic acid liberated at the anode is very small compared with the weight of water in the anode portion, and this correction is relatively unimportant.

TABLE I

| Concentrations | | | Coulometers | | Anode portion | | Transport number of cation |
|----------------|--------------|----------------|-------------|---------|---------------|--------|----------------------------|
| initial | anode-centre | cathode-centre | anode | cathode | weight | nickel | |
| 0.2046 | 0.2045 | 0.2045 | 0.3747 | 0.3743 | 26.85 | 0.2417 | 0.573 |
| 0.1962 | 0.1961 | 0.1962 | 0.3784 | 0.3786 | 28.99 | 0.2553 | 0.566 |
| 0.1718 | 0.1717 | 0.1715 | 0.3454 | 0.3452 | 29.61 | 0.2265 | 0.582 |
| 0.1718 | 0.1717 | 0.1721 | 0.3532 | 0.3532 | 30.98 | 0.2382 | 0.581 |
| 0.1510 | 0.1509 | 0.1510 | 0.4749 | 0.4748 | 78.35 | 0.5833 | 0.589 |
| 0.1080 | 0.1080 | 0.1080 | 0.2943 | 0.2941 | 82.53 | 0.4569 | 0.589 |
| 0.1080 | 0.1079 | 0.1079 | 0.2952 | 0.2954 | 75.65 | 0.4148 | 0.589 |
| 0.0702 | 0.0702 | 0.0702 | 0.4015 | 0.4014 | 72.40 | 0.2253 | 0.602 |
| 0.0496 | 0.0497 | 0.0498 | 0.2567 | 0.2568 | 71.69 | 0.1623 | 0.612 |
| 0.0496 | 0.0494 | 0.0496 | 0.2807 | 0.2810 | 67.76 | 0.1475 | 0.605 |
| 0.0306 | 0.0306 | 0.0307 | 0.1573 | 0.1576 | 76.35 | 0.1095 | 0.610 |
| 0.0306 | 0.0306 | 0.0305 | 0.1730 | 0.1738 | 72.72 | 0.1007 | 0.605 |
| 0.0195 | 0.0195 | 0.0193 | 0.1148 | 0.1148 | 77.25 | 0.0683 | 0.617 |
| 0.0195 | 0.0193 | 0.0195 | 0.1082 | 0.1082 | 71.65 | 0.0631 | 0.614 |
| 0.0192 | — | 0.0191 | 0.0864 | 0.0864 | 72.07 | 0.0661 | 0.612 |

The results obtained are given in Table I: columns 1, 2, and 3 give, respectively, the initial concentrations and the concentrations of the anode centre and the cathode centre portions, in mols per 1000 gm. water: columns 4 and 5 show the increase in weight in grams of the cathodes of the two silver

coulometers: in columns 6 and 7 are the weights and nickel contents in grams of the anode portion removed after the experiment, and in the last column are the calculated values of the transport number of the cation.

Discussion

Neither the mobility of the nickel ion, nor that of the salicylate ion has been determined accurately. The most reliable value for the nickel ion at 25° C. appears to be that of Heydweiller¹ —52.1. The only determination of that of the salicylate ion is by Prideaux and Crooks² who give the value 36. From these figures the transport number of the cation in nickel salicylate should be 0.591: the difference between this value and our determinations is fully accounted for by the uncertainty of the mobilities. The agreement, such as it is, shows nickel salicylate to be ionised mainly as a normal nickel salt.

From the recorded experimental data³ and on the basis of modern theories of conductivity⁴, it follows that, where a transport number is influenced by concentration its value tends to increase with diminishing concentration when it is less than 0.5, and to decrease with diminishing concentration when it is higher than 0.5. It will be seen, therefore, from Table I, that the change with concentration in the transport number of the cation in aqueous solutions of nickel salicylate is unusual.

We believe this abnormality can be explained by the presence in the more concentrated solutions of a small amount of the acid form of nickel salicylate — $H_2[NiSal_2]$ (or possibly $H[HSalNiSal]$) — for the presence of this anionic nickel should affect the transport numbers in the observed manner. The existence of such compounds⁵ as $K_2[NiSal_2]$ shows that nickel salicylate can react, and must be present to some extent in solution, as an acid; and, as was shown for the copper compound, the relative proportions of acid form to salt form should increase with concentration. Obviously, only a small proportion of nickel is present as complex ion even in the most concentrated solutions; this fact, and uncertainty as to the mobilities of the various ions, preclude any attempt to evaluate quantitatively the equilibrium constant.

A series of confirmatory experiments was undertaken by Mr. W. E. Hamer, in which salicylic acid was determined analytically in the anode portion. The most suitable method of determining this was found to be that recommended by Prideaux and Bentley.⁶ It was realised that all analytical methods were too crude for the results, which are given in Table II, to have much value; but these do give a rough confirmation of the more accurate de-

¹ *Z. physik. Chem.*, 89, 285 (1914); see, however, Althammer: *Diss. Halle* (1913) quoted by Heydweiller; and Rona: *Z. physik. Chem.*, 95, 62 (1920).

² *Trans. Faraday Soc.*, 20, 37 (1924).

³ See Noyes and Falk: *J. Am. Chem. Soc.*, 33, 1436 (1911), especially Table V.

⁴ Onsager: *Trans. Faraday Soc.*, 23, 341 (1927); Davies: *J. Phys. Chem.*, 29, 473 (1925).

⁵ Barbieri: *Atti. Acad. Lincei*, 25 II, 75 (1916).

⁶ *Pharm. J.*, 110, 427 (1923).

TABLE II

| Mols salt per 1000 gm. water | Transport number of cation | Mols salt per 1000 gm. water | Transport number of cation |
|---------------------------------|-------------------------------|---------------------------------|-------------------------------|
| 0.0679 | 0.59 | 0.0338 | 0.57 |
| 0.0679 | 0.62 | 0.0225 | 0.59 |
| 0.0338 | 0.63 | 0.0225 | 0.58 |

terminations given in Table I, and justify the statement made above that one mol of salicylic acid per faraday is liberated at the anode.

Summary

Transport numbers in nickel salicylate solutions at 25°C. have been determined throughout the range 0.02 to 0.2 (the limit of solubility) mols per 1000 gm. water. The results show that nickel salicylate ionises mainly in a normal manner, but also suggest the presence of small amounts of a complex acid form.

One of us (F.E.J.) wishes to acknowledge his indebtedness to the senate of this college for the award of a Garrod Thomas fellowship.

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March 19, 1928.*

NEW BOOKS

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. By J. W. Mellor. Vol. VIII. 25 × 17 cm; pp. x + 1110. New York and London: Longmans, Green and Co., 1928. Price: \$20.00. This volume deals with nitrogen and phosphorus and increases our debt of gratitude to the author. As usual, there are many interesting items. On p. 2 there is a reference to Rice's work on the catalytic action of suspended dust. E. Dubois estimates that about six million kilograms of salt are precipitated annually by rainfall on two provinces of Holland, p. 12. Mellor accepts McLennan's view, p. 31, that the green line of the aurora is due to oxygen and not to nitrogen.

"It is difficult to state precisely who first isolated nitrogen and clearly recognized it as a definite substance. In his experiments on combustion or burning, John Mayow, during his investigation on nitre, got very near, if he did not get actually there. Several others also were not far away from the discovery. As G. F. Rodwell pointed out, the man who deduces on good mental evidence, or even proves by actual experiment, the existence of something not known before is not always recognized as the discoverer; but rather is hailed discoverer he who proves by a conclusive series of experiments that the substance in question has properties, *sui generis*, distinct from all other substances. *He alone discovers who proves.* Otherwise, Boyle or Paracelsus would be called the discoverer of hydrogen; Lucretius, of carbon dioxide; J. Kunckel, of ammonia; Eok de Sultzbach, of oxygen; Hooke or Cassini, of the law of gravitation; etc. D. Rutherford is generally credited with the discovery of nitrogen," p. 45.

On p. 51 is the statement that azides decompose slowly in vacuo, giving off nitrogen. On the preceding line is the item that Saarvasy obtained nitrogen by electrolysis of hydrazine; but there is nothing to show at which electrode. On p. 119 is the suggestion that titanium nitride may be the pigment in the amethyst.

"Soils readily adsorb gases of various kinds, and the occurrence of ammonia in soils has been discussed by Knop, Mayer, Müntz and Coudon, Marchal, and Berthelot and G. André. The ammonia is derived from the decomposition of nitrogenous matter in the soils. Ehrenberg has discussed *Der Kreislauf des Ammoniakstickstoffs in der Natur*. Gmelin observed that ammonia is given off when some minerals are calcined. Bouis noted that most clays contain some ammonia. The ammonia in clays and ferruginous ores is supposed to have been absorbed from the atmosphere and partly derived from the oxidation of iron in contact with air and moisture. Faraday showed that clay, which has been heated to redness, absorbed an appreciable quantity of ammonia from the air during eight days' exposure. Boussingault found that ferric oxide from the middle of a deep boring near Marmato contained ammonia. The presence of ammonia in iron ores, dolomite, clay, soil, and other porous substances has been noted by Vauquelin, Chevallier, Faraday, Bouis, Knop, Mayer, Dieulafait, and Austin. The occurrence of ammonia in iron-rust was noted by Bourdelin in 1683, and later, by Vauquelin, Chevreul, and Reiset; and Barré, and Regnard detected an odour of ammonia on breaking several ingots of steel, prepared by a special process, and gas escaped accompanied by a slight hissing noise. Analyses showed that the gas is mainly hydrogen and hydrocarbons—no ammonia or nitrogen was detected," p. 147.

Ammonia goes through rubber eight times as rapidly as hydrogen does, p. 200. Somebody should study the taking-up of ammonia by cyclohexane because a liter of this substance is said to dissolve twenty-eight liters of ammonia at 26° and 755 mm.

"Werner's hypothesis seems to give a clearer insight into the constitution of double salts, complex salts, crystalline hydrates, etc., than any yet propounded; and it forms the most elegant system yet proposed for classifying large groups of complex compounds, and particularly the ammonia metal bases. Although it is fully recognized that this hypothesis has not assumed its final form, yet, as one of the fathers of philosophy has said, we begin with

doubts in order that we may end with certainties; and there is the promise that the conception of molecular compounds as something specifically different from atomic compounds will ultimately be banished from chemistry," p. 233.

On p. 309 are the statements that hydrazine is a direct reduction product of hyponitrous acid and that the presence of a sulphite is usually necessary for the reduction. These two statements seem to be somewhat contradictory. Glauber is quite eloquent on the subject of potassium nitrate, p. 356.

"Deservedly may saltpetre or nitre be termed the universal subject and wonder of the world. . . . If it were not so, how comes it to be so plentifully found in all things? . . . All these things which dung the fields and lands, and fatten them most necessarily contain in them saltpetre; for, from this only and alone, comes all the fertility throughout the whole earth, which axiom cannot be gainsayed. . . . Having shown that nitre or saltpetre may be had from all things, viz., from herbs, wood, four-footed beasts and creeping things, from birds in the air, and fishes in the water, yea, from the very elements themselves—earth, water, air, and fire—it must needs follow that it is that so much spoken of universal spirit, without which nothing can either be or live. It is the begetter and destroyer of all things, as I have demonstrated in my *Miraculum mundi* out of the most ancient philosopher Hermes. I therefore hope that nobody will any more doubt thereof or oppose himself with a perverse stubbornness against a truth so manifestly known. . . . If any one is minded firmly to cleave to his own stubborn perverseness, even Hermes himself, should he rise from the dead, would lose his labour in teaching him."

When hydrogen, methane, ethylene, or propylene is burned in an atmosphere of nitrous oxide, "the hydrocarbons give a core of white light with an apricot-coloured, and then a large, greenish-grey sheath. The flames are magnified roughly five times in height and twice in diameter. No peroxide could be detected in the interconal gases, but it is found in the gases of the outer flame," p. 395. It is possible to read by the hydrogen flame in nitrous oxide, though the one in air is almost non-luminous.

According to Burt and to Usher there is an allotropic nitrogen sulphide, a film of which is blue by transmitted light and bronze with a metallic lustre in reflected light, pp. 627, 629. Frémy oxidized a solution of potassium hydroxynitrosulphonate with silver oxide or lead dioxide and obtained a solution with an intense violet-blue color, from which golden-yellow crystals separated, p. 684.

"Phosphorus is nearly the most widely and evenly distributed element on the surface of the earth, and probably the most subdivided. This can be readily understood when the important part which phosphoric acid plays and has played in the vital cosmos is taken into consideration. Phosphorus was on the earth in gaseous, liquid, or solid form before the dawn of life, and since then, all animal and vegetable creations have combined with the physical forces always at work in inanimate nature to distribute and redistribute the phosphorus, to divide it up, and carry it from place to place. If the biography of atoms could be written, the chapters on phosphorus would be the most interesting and the most varied," p. 732.

"Dry bones, on the average, contain the equivalent of about 60 per cent. of tricalcium phosphate; teeth, 70 per cent.; crab and snail shells, 7 per cent. When the animals die, their remains help to build up phosphate rocks. Thus, the story of the circulation of phosphorus is a cycle of processes involving the concentration and dissipation of that element. The waste of muscular and nervous tissue involves a decomposition of the phosphorus compounds. The products of decomposition are carried by the blood to the kidneys, and there excreted with the urine—chiefly as sodium ammonium phosphate. There seems to be a relation between the amount of phosphorus compounds discharged from the system, and the activity of the brain, and this led to the inference that phosphorus is a metabolic product of the activity of the brain, and that phosphate foods are needed for brain workers. The idea has crystallized in the well-known phrase *ohne Phosphor kein Gedanke*—without phosphorus no thought. A similar statement might be made regarding several other elements. A normal adult excretes the equivalent of 3 to 4 gms. of phosphoric acid *per diem*. Part of this is derived from the food, and part from muscular waste. In this way, phosphorus

finds its way back to the soil; or perhaps into the sewage, and finally into the sea. Lindgren thus describes the fate of the phosphorus which finds its way into the sea."

"In the sea-water the blue-green algae concentrate phosphorus, certain molluscs, or crustaceans, feed on the algae, and other meat-eating molluscs devour the vegetarians. Small fishes eat the molluscs, large fishes eat the small, finally seals and birds swallow the fishes, and so in about six transformations the phosphorus originally contained in the sea-water may come to rest in deposits of guano on desert islands or in accumulations of the bones of the vertebrate denizens of the sea. Hence the origin of the phosphorus in the large deposits of guano—the excrement of sea-birds—on the islands off the Peruvian coast, and a number of islands in the South and the Caribbean Seas. Many islands have been stripped of the guano they once contained. The amount of phosphates returned from the sea as edible fish is insignificant in comparison with what is drained into the sea as sewage from towns. Processes for the recovery of the phosphates in sewage now attract attention, since that which escapes into the sea accumulates at the bottom, where it may be unproductive for countless ages before it is again able to take an active part in nature's great cycle of changes. The constant growth of crops by the farmer impoverishes the soil, and phosphatic manures are needed to make good the loss," p. 737.

Mellor considers that there are only four allotropic forms of phosphorus, the α - and β -forms of yellow phosphorus, red or violet phosphorus, and black phosphorus, p. 749. The triple point for red phosphorus, liquid phosphorus, and vapor at 589.9° and 43.1 atmospheres, seems more accurate than the experiments. The α -yellow phosphorus melts at 44.1° and changes to β -yellow phosphorus at -76.9° .

"The curious natural phenomenon known as *ignis fatuus* (*ignis*, fire; *fatuus*, wild, silly), or in France *feux follets*, often manifests itself as more or less transient, flickering, "light, spirituous flame dancing on the heath," and it has been frequently reported to appear in darkness over peat-bogs, swamps, marshy districts, lagoons, damp cemeteries, recent battle-fields, stagnant waters, etc. The *ignes fatui* were at one time thought to be manifestations of the supernatural, and were called in Scotland *elf-candles* or *elf-fire*—in allusion to the elves or mischievous sprites which the superstitious believe haunt the wild places where the phenomenon usually occurs; in Wales, *corpse-candles*—in reference to their frequent appearance in cemeteries; and in England, *Jack-o'-lanterns* or *Will-o'-the-wisps* in allusion to rustic fairy tales. Some rather brilliant displays have been reported at various times. The phenomenon is not to be confused with the light from luminous insects hovering over marshy grounds. The general idea is that the *ignes fatui* are due to the spontaneous ignition of bubbles of gas containing traces of phosphuretted hydrogen evolved, along with other gases, during the decomposition of animal substances under water or in damp soils. Bubbles of gas no doubt escape in the day as well as at night, but the feeble light which is emitted when a gas bubble containing a little phosphuretted hydrogen comes in contact with the air, is visible only in dusk or in darkness," p. 803.

Wilder D. Bancroft

Outlines of Theoretical Chemistry. By Frederick H. Getman. Fourth edition. 22 × 16 cm; pp. xiii + 728. New York: John Wiley and Sons, 1927. Price: \$3.75. In the preface to this edition the author says, p. V. "Among the more important changes to be noted in the present edition, the following may be mentioned:—A fuller treatment of limiting densities and vapor pressures; a brief description of the latest and most accurate method of measuring heats of vaporization; a more comprehensive treatment of crystal structure and the methods of X-ray analysis; an enlargement of the section treating of the absorption of light and its bearing on chemical constitution; a thorough revision of the chapter on the elementary principles of thermodynamics; a more discriminating treatment of the phenomena of osmosis; the inclusion of the concepts of fugacity and activity in connection with the subject of vapor pressures of dilute solutions; a fuller discussion of the theories of emulsification and gel formation; an enlargement of the sections devoted to adsorption and the methods of preparation of colloids; a more detailed account of the theories of catalysis; the treatment of the more important practical applications of conductance and electrometric methods in

separate sections in the respective chapters devoted to electrical conductance and electromotive force; the simplification of the treatment of hydrolysis; the adoption of a uniform and consistent system for the representation of galvanic cells, thereby connecting their polarity with the direction of current flow, a fuller treatment of both the hydrogen electrode and oxidation and reduction cells; the rearrangement and enlargement of the chapter on electrolysis and polarization; a brief presentation of the quantum theory together with its application to the principle of photochemical equivalence; an outline of Baly's fascinating and suggestive researches in the field of photosynthesis; and lastly, the complete revision of the chapter on atomic structure."

The treatment is quite modern. Osmotic pressure is discussed from Washburn's point of view, essentially as a kinetic phenomenon, p. 213. Raoult's law is considered as a special case of Henry's law, p. 234, in spite of the fact that Henry's law is a relation for the same substance in vapor and solution, while Raoult's deals with the vapor pressure of one substance and the concentration of the other. There is also nothing to show to what the molecular weights refer in Raoult's law. That does not matter for ideal solutions, because the molecular weights are the same in both phases by definition.

Fugacity is introduced on p. 237 and activity on the bottom of the next page. The author stands out, however, against one hundred percent dissociation. The classification of colloids is that of von Weimarn and Wolfgang Ostwald; but the author talks about emulsoids and suspensoids, p. 315. Adsorption is taken up thirty-five pages later, which means that the treatment in the intervening pages is necessarily empirical. The author follows the modern practice and writes $Zn | ZnSO_4 = -0.797$ volts, p. 546. He is a bit non-committal about the theory of over-voltage, p. 606.

"All of the dyestuffs which can function as optical sensitizers have been found to exhibit anomalous refraction, i.e., for wave-lengths slightly longer than those absorbed, these substances possess an abnormally large refractive index, in consequence of which the refracted waves exert the same effect upon the silver halide as the shorter wave-lengths of the spectrum. Although it is not an essential property, it is generally found that optical sensitizers are fluorescent," p. 643.

The author is not so modern that he does anything with the displacement of the water equilibrium or that he refers osmotic pressure to the volume of the solvent rather than to the volume of the solution; but these things will come in some future edition.

Wilder D. Bancroft

Photometric Chemical Analysis. By John H. Yoe. Volume I. *Colorimetry*. 23 × 15 cm; pp. xxi + 771. New York: John Wiley and Sons, 1928. Price: \$8.50. "The great demand in all fields of applied chemistry is for analytical methods of sufficient accuracy which require but little time for completion. In recent years another requisite has been added to that of sufficient accuracy and rapidity, namely that of sensitivity, so that extremely small amounts of substance can be analyzed or determined if necessary." "The rapid growth of colorimetry and nephelometry has created a demand for a comprehensive reference work on these two methods of chemical analysis" and the author believes "that the time is not ripe for the theoretical consideration and correlation that these two sister methods of chemical analysis deserve."

"Photometric chemical analysis may be defined as analysis which depends upon a change in the amount or character of light due to a chemical reaction. The change in the amount of light as understood in this treatise is that due to either absorption or reflection. Analysis made on the basis of absorption is usually called colorimetry, and in a few cases turbidimetry, while analysis based on reflected light is called nephelometry."

The author discusses the different methods employed in matching colors and the requirements of a satisfactory colorimetric method.

"No general statement can be made as to the accuracy of colorimetric methods. Some colorimetric determinations have been brought to such a high degree of perfection that they far surpass gravimetric or volumetric determinations in accuracy. On the other hand, many colorimetric methods are only rough approximations."

"As in the case of accuracy, colorimetric methods vary widely from the standpoint of speed. Some are extremely rapid, requiring only a few minutes, while others are slow and tedious, especially if the highest degree of accuracy is desired. Often accuracy is sacrificed for speed."

"In general a colorimetric method cannot be used when more than one or two percent of the substance being determined is present without resorting to aliquot parts" and "they are applicable to concentrations of one or two percent down to one part in a hundred million but these limits may be extended under the proper conditions."

Following a complete description of the various forms of colorimetric apparatus, the author discusses the methods of calculating results, the calibration of colorimeters and correction curves.

"In all colorimetric methods, it is stated or implied that Beer's law is valid but this law does not hold in many cases. Therefore in all colorimetric methods such influences must be recognized, the limits of dilution must be set, and comparisons made under identical conditions," p. 88.

Numerous possible errors in colorimetry are pointed out but "fortunately, however, most of these errors can be avoided or reduced to a satisfactory minimum by carefully worked-out procedures and good technique, together with the use of a good colorimeter or carefully matched color comparison tubes," p. 89.

The first part of the book is concluded with a discussion of the use of colored colloid suspensions, colorimetric stabilizers and general directions for using a precision colorimeter.

The major portion of the book is devoted to detailed directions for making many inorganic, organic and biological determinations. The author has endeavored as far as possible to state the limits of accuracy of each method.

The book is replete with references to the original literature and an extensive bibliography, arranged alphabetically by subject and chronologically under each subject, has been included.

In the opinion of the reviewer, the author has covered the subject of colorimetry not only fully but exceptionally well and it can be recommended both for the advanced student in chemistry and for the research worker as well, who may have occasion to make use of colorimetric methods of analysis.

M. L. Nichols

Mikrophotographie. By August Köhler. *Lieferung 245, Abderhalden's Handbuch der biologischen Arbeitsmethoden.* 24.5 × 17.5 cm; pp. 287. Berlin: Urban and Schwarzenberg, 1927. Price: 10.80 marks. As an exhaustive treatise on the theory of photomicrography, this book is perhaps unique. It is written in the typical *Handbuch* style, with chapters and subchapters on all phases of photomicrographic procedure. This does not make a very readable work, but facilitates reference to the different sections, and since there is no index to this *Lieferung*, such a systematic arrangement is very important. The three main divisions are: Photomicrography with Visible Light; with Ultra-violet Light; and Stereoscopic Photomicrography. The first of these deals very completely with the general principles of illumination which are so important in governing the interpretation of microscopic structures. Lens equipments for various purposes are discussed in detail, as are a number of different photomicrographic cameras. Unfortunately, the emphasis is almost entirely on Zeiss apparatus and the manipulative methods appropriate to it are given in great detail, at the expense of descriptions or comparisons of instruments by other makers.

The operations of photography are treated very completely, and with special reference to purely photomicrographic problems such as choice of exposure, correct rendition of values, and photomicrography of colored objects.

Although a general understanding of the theory of the microscope is presupposed, the author deals rather fully with the diffraction theory of resolution, and its application to ultra-violet microscopy.

Mikrophotographie is to be recommended highly as a supplement to the more elementary books on this subject, and, together with *Das Mikroskop und seine Anwendung* (Lief. 95) also by Köhler, it constitutes a valuable addition to the writings on critical microscopy.

C. W. Mason

THE ELECTRICAL CONDUCTIVITY OF TELLURIUM AND OF LIQUID MIXTURES OF TELLURIUM AND SULPHUR

BY CHARLES A. KRAUS AND ERNEST W. JOHNSON

I. Introduction

The immediate purpose of the present investigation was to determine the influence of varying amounts of sulphur on the electrical conductivity of metallic tellurium. According to the literature¹ sulphur and tellurium are miscible in all proportions in the liquid state and the phase diagram indicates an absence of compounds between the two components. Since tellurium is a metallic conductor and sulphur is a non-conductor, it appeared of interest to investigate the conduction process in mixtures of these two elements as a function of composition. Solutions of metals in non-metallic solvents occur only infrequently. The only systems of this type that have been studied extensively are solutions of the alkali metals in liquid ammonia.² In these solutions the metallic atom appears to be ionized into a normal positive ion and an electron which is more or less associated with the solvent molecules. In a mixture, such as tellurium and sulphur, it might be anticipated that the relation between conductivity and composition would vary greatly from that of the ammonia solutions just mentioned. Tellurium itself is only very weakly electropositive and has a relatively high affinity for the electron. Sulphur has a low dielectric constant and we should expect that, in a mixture of sulphur and tellurium, the conducting power would fall rapidly with increasing concentration of sulphur. Moreover, since sulphur has a high affinity for electrons, we might expect that at higher concentrations (of sulphur) the electrons would associate themselves with sulphur atoms or molecules and that the conduction process would be of the electrolytic type. Such, in fact, has been found to be the case. Incidentally, the conductivity of pure tellurium has been measured for the solid as well as the liquid state.

The method employed in measuring the conductivity of pure tellurium as well as that of its mixtures with sulphur consisted in introducing the tellurium, or its mixture with sulphur, into suitable cells whose constants had been determined. The cells containing the materials were introduced into a thermostat whose temperature was readily varied and controlled. The mixtures were melted under an atmosphere of nitrogen. The resistance of the mixtures was measured by means of a direct current and Wheatstone bridge or an alternating current and Kohlrausch bridge.

II. Materials, Apparatus and Procedure

Tellurium. The tellurium was prepared according to the following procedure: An impure metal was dissolved in nitric acid in the presence of a

¹ Pellini: *Atti. Acad. Lincei*, 18 I, 701 (1909); Chikashige: *Z. anorg. Chem.*, 72, 109 (1911); Jaeger and Menke: 73, 241 (1912).

² Kraus: *J. Am. Chem. Soc.*, 53, 749 (1921) and earlier papers; Kraus and Lucasse: 43, 2531 (1921); 44, 1941 (1922); 45, 2551 (1923).

small amount of hydrochloric acid and evaporated to dryness. The residue was heated to decompose any traces of basic nitrate, hydrochloric acid was added and the product was again evaporated to dryness in order to remove all traces of nitric acid. This product was dissolved in strong hydrochloric acid, diluted with hot water, made slightly alkaline with ammonia and acidified with dilute acetic acid. The tellurium dioxide precipitated in this operation was thrown on a filter, washed and dried. It was then heated to 750° in an alundum boat in a quartz tube with a slow stream of oxygen passing

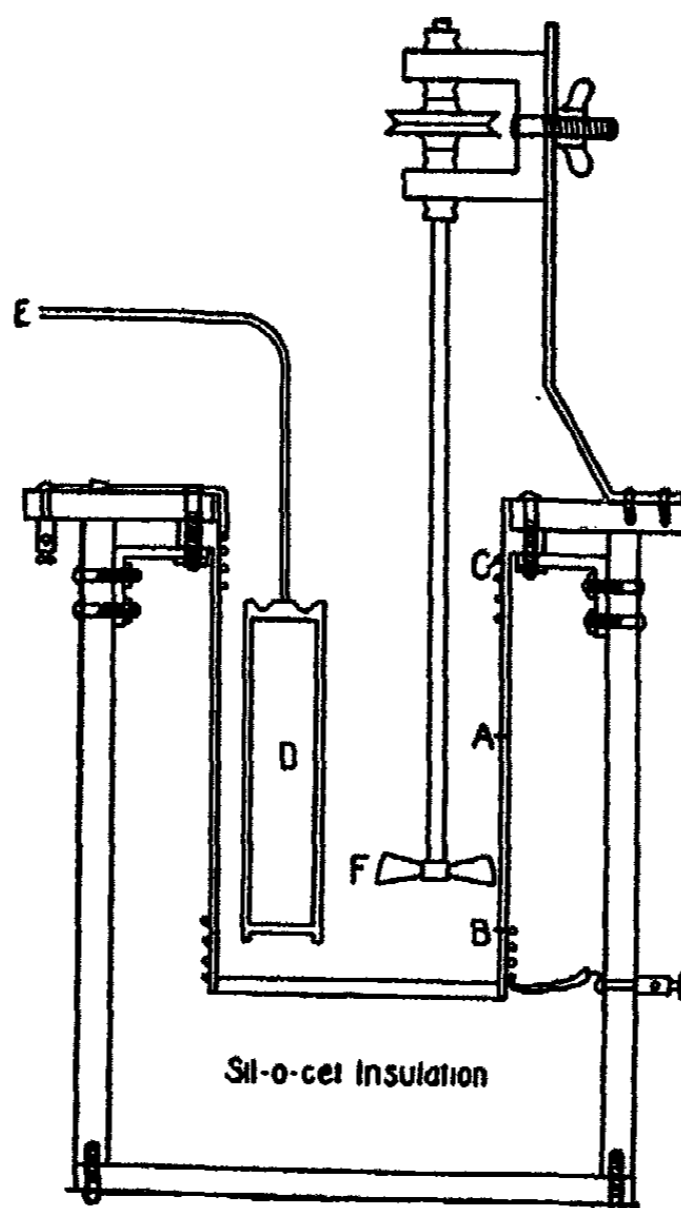


FIG. 1
Thermostat

over it. This served to remove the greater proportion of selenium dioxide present. The resulting product was dissolved in strong hydrochloric acid, the solution diluted to about 6 N, and the metal reduced by means of sulphur dioxide at a temperature of about 90° . The precipitated metal was thrown on a filter, thoroughly washed with water and finally with alcohol. After drying in a vacuum desiccator, the metal was distilled in vacuo from an alundum boat placed in a pyrex tube. The final product gave no qualitative test for probable impurities including selenium.

Sulphur. Sulphur was purified by recrystallization from freshly distilled carbon bisulphide.

The Thermostat. The resistance temperature coefficient of the various mixtures was found to be high and it was therefore necessary to provide means for accurate and convenient temperature control of the thermostat in which the cells containing the mixtures were placed. The thermostat con-

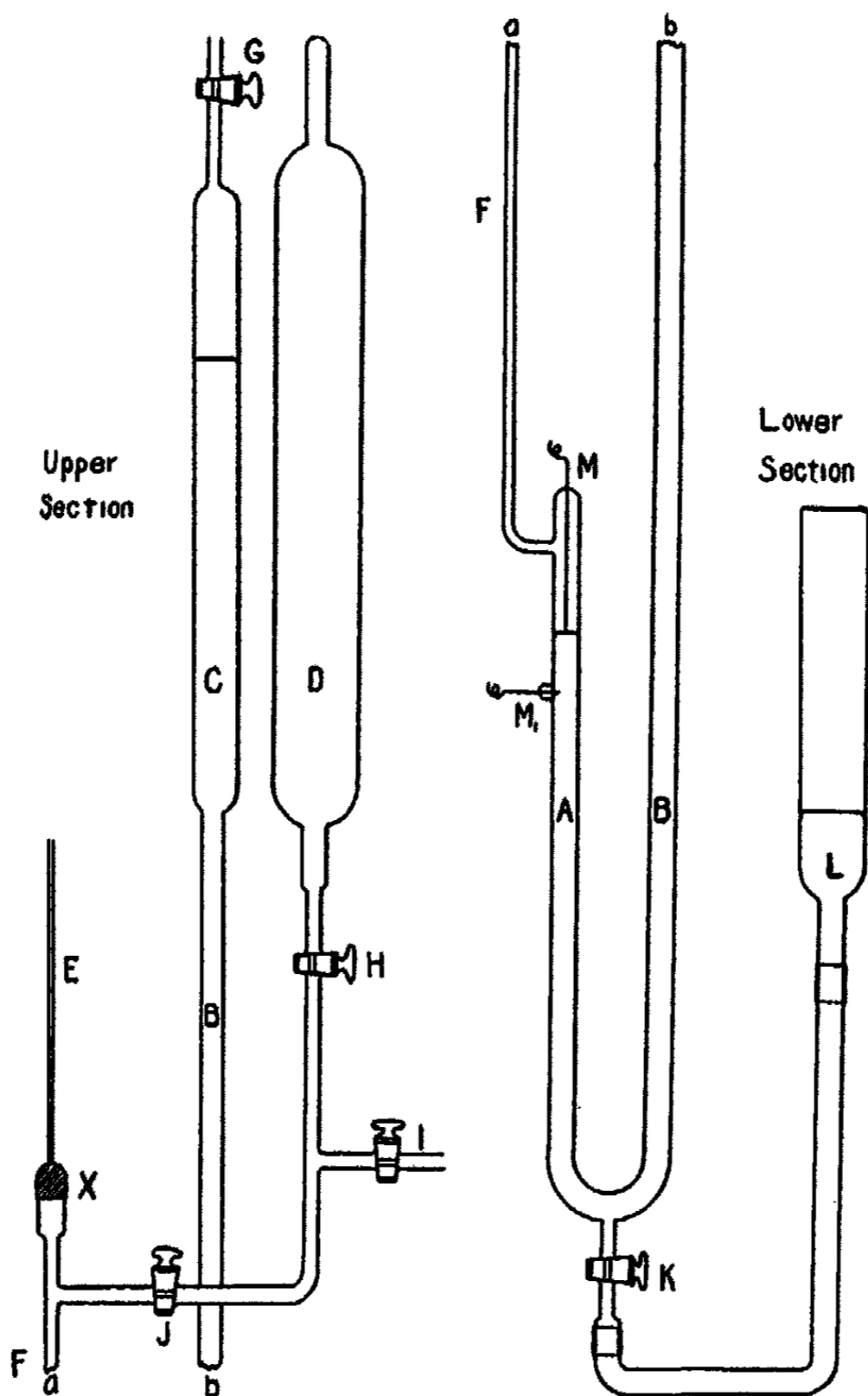


FIG. 2
Temperature Regulator

sisted of a welded metal pot *A* (Fig. 1) in which a low melting lead-tin alloy was employed as thermostatic liquid. The pot was wound on the outside with nichrome wire *B*, a current through which served to compensate for radiation loss or to heat up the thermostat initially. The pot was lagged with sil-o-cel contained in an asbestos board box. The liquid in the thermostat was thoroughly stirred by means of a motor-driven propeller *F*. Within

the pot, and underneath the surface of the thermostatic liquid, was placed an armored resistor *C* wound in the form of a helical spiral just slipping into the pot. Through this coil was sent an intermittent current which served to maintain the temperature of the thermostat at a constant value. The make and break of the regulating current was effected by means of a constant volume gas thermometer. This thermometer consisted of a thin walled steel tube *D*, having a diameter of 4 cm. and a length of approximately 15 cm., all joints being welded. This bulb was connected with the electrical contact device by means of a small steel tube *E*, (Figs. 1 and 2). This tube had a thickness a little under 1 mm. and a diameter of approximately 3 mm.

The regulating device is outlined in Fig. 2. The steel thermometer bulb was attached to tube *F* of this device by means of a deKhotinsky seal at *X*. Tube *F* was connected with a mercury column *AB*. The height of mercury in this column was adjustable by means of a movable reservoir *L* and could be fixed by closing the stopcock *K*. The free space above the mercury column *C* was exhausted through stopcock *G*. The regulator, including the thermometer bulb, could be exhausted through stopcocks *I* and *J*. Initially, the mercury was lowered in the reservoir *L* until connection between the arms *A* and *B* was established after which the stopcock *K* was closed. The thermometer bulb was then exhausted through *I* and filled with nitrogen at a pressure of approximately $1\frac{1}{4}$ atmospheres. Stopcock *K* was then opened, *C* was exhausted through *G* and the mercury level was adjusted to make contact with the platinum point *M* at the desired temperature in the thermostat. Stopcocks *J* and *I* were then closed. The diameter of the tube *A* was approximately 8 mm. The chamber *C*, in which was located the upper level of the mercury column, had a diameter of approximately 2 cm. The purpose of this was to increase the sensitivity of the contact device. The free volume of the tube above the mercury surface *A* was made as small as possible, while the connecting tubes *E* and *F* had an internal diameter of about 2 mm. The object of this was to reduce the external volume to a minimum so as to increase the sensitivity as well as to improve the constancy of the regulator. Tube *D* was a chamber filled with nitrogen in the initial filling. By opening stopcocks *H* and *J*, this reservoir could be connected with the thermometer bulb when it was necessary to allow the thermostat to cool down to comparatively low temperatures. To change the temperature setting of the thermostat, the temperature was raised to approximately the desired point, stopcock *K* was opened and the level of the reservoir *L* adjusted until contact was made with the platinum point at *M*. On closing stopcock *K*, the existing temperature was automatically maintained.

The device above described proved to be extremely convenient and reliable at temperatures from 200°–600°. The temperature of the thermostat was read by means of a platinum, platinum-rhodium thermocouple and regulation was effective to 0.1°, as indicated by the couple. To prevent oxidation of the alloy in the thermostat at higher temperatures, a thin layer of powdered graphite was placed over it.

Conductivity Cells. Two types of conductivity cells were employed depending upon the specific resistance of the mixture. The first type, illustrated in Fig. 3, consisted of a pair of platinum wires having a diameter of about 0.7 mm. and a length of 5 mm. sealed through a Pyrex tube *A*. These wires were joined to a pair of copper leads *F* passing through a rubber stopper *D*. The electrode tube *A* was inserted in a Pyrex tube *B*, into which it fitted closely, closure of the junction being effected by means of a short length of pure gum tubing *C*. The relative position of the tubes was carefully gauged, since the constant of the cell depended slightly upon the position of the electrodes. The interior of tube *A* was connected with the interior of *B* through a small opening *G* in order to prevent the passage of the melted mixture into the interior of *A* along the platinum wires. At the bottom, the electrode tube *A* was provided with a loop of glass rod *E*. The purpose of this was to facilitate the stirring of the mixture which was accomplished by turning the tube *A* through an angle.

These cells were calibrated by comparison with a standard cell of the pipette type. A solution of potassium iodide, nearly saturated with iodine, was employed in making the comparison. The presence of the iodine eliminates polarization and makes it possible to determine the cell constant of unplatinized electrodes. The resistance of the leads was determined by dipping the electrodes into mercury and measuring the resistance by means of a precision bridge. The cell constants and the data from which these constants were derived are given in Table I.

TABLE I
Lead Resistances and Cell Constants for Cells used in measuring the Resistance of Mixtures rich in Sulphur

| Cell No. | R. | Lead R. | R. (Corr.) | Cell Const. |
|------------------------------|-------|---------|------------|-------------|
| 4 | 296.9 | 6.9 | 290.0 | 3.442 |
| 5 | 141.9 | 5.4 | 136.5 | 1.620 |
| 6 | 216.6 | 6.1 | 210.5 | 2.449 |
| 7 | 207.6 | 5.1 | 202.5 | 2.404 |
| 8 | 175.1 | 6.0 | 169.1 | 2.007 |
| Pipette Cell (comparison) | 286.7 | 0.4 | 286.3 | 3.397 |

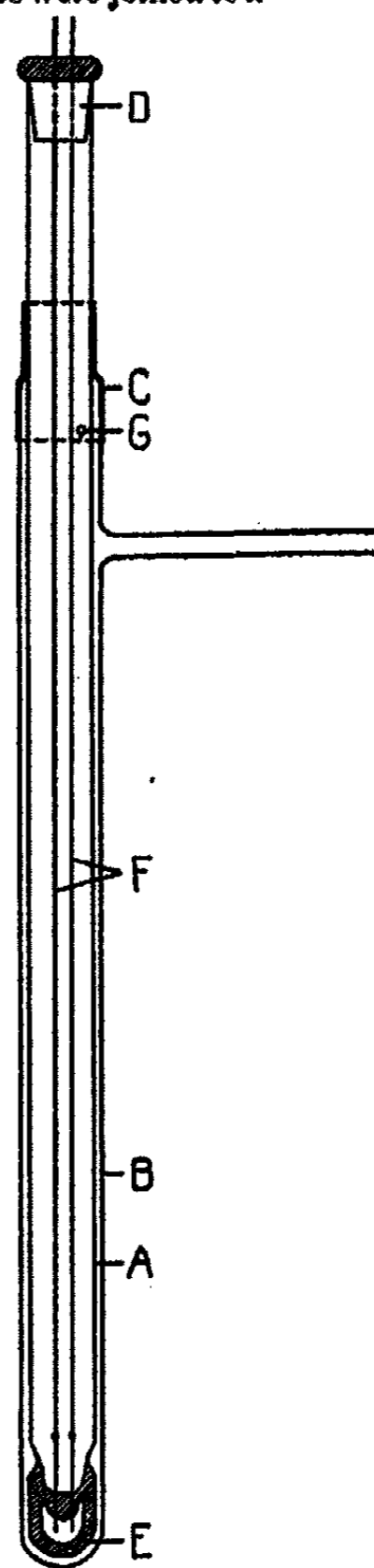


FIG. 3
Cell for measuring conductance of mixtures of S and Te rich in S.

For measuring the resistance of tellurium and of mixtures rich in tellurium, it was necessary to use a cell having a high resistance capacity. Such a cell is outlined in Fig. 4. Two arms, *KK* are joined by a length of capillary tubing *AA* having an internal diameter of about 1 mm. Platinum leads *BB*

are joined to copper conductors and sealed into tubes *CC*. The platinum points are adjusted to make contact with the metal at the ends of the capillary *AA*. The mixture to be melted is introduced into tube *D* which connects with the capillary *AA* by means of tube *L*. Closely fitting in tube *D* is a plunger (not shown in the figure) reaching to the bottom of that tube. This plunger can be raised or lowered at will by slipping through a rubber connection at the top of tube *D*. After introducing the metal into tube *D* and

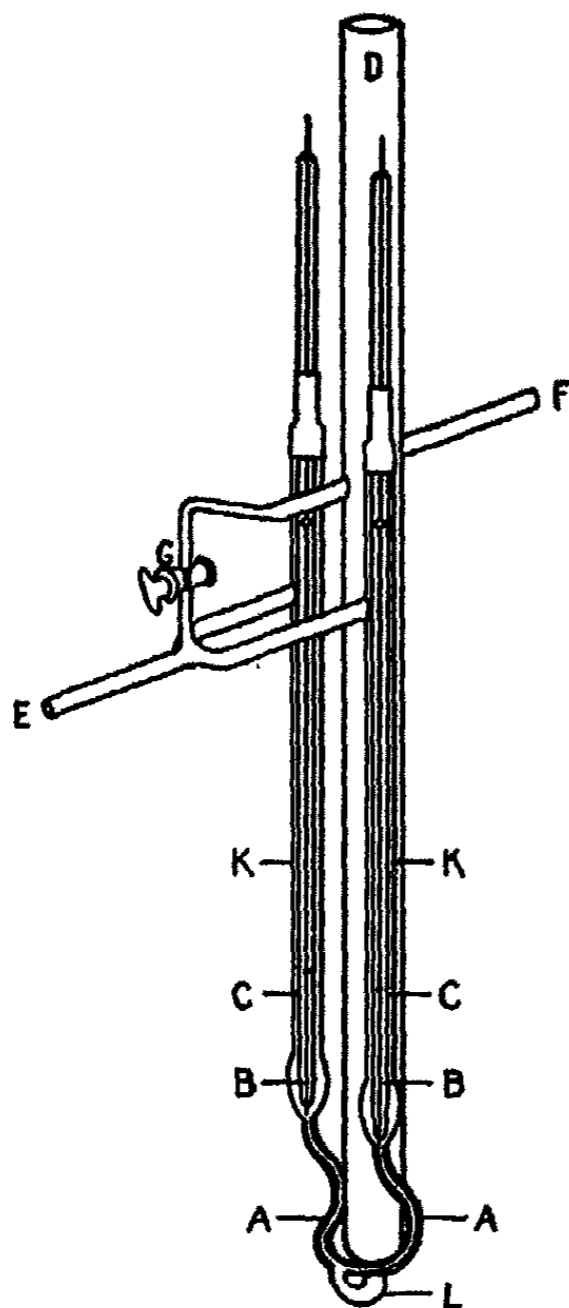


FIG. 4
Cell for measuring conductance of mixtures of S and Te rich in Te.

filling with nitrogen, the cell is placed in the thermostat and, when the material in *D* is melted, the plunger is lowered to the bottom forcing the melt to pass through tube *L* and through capillary *AA* making contact with the electrical circuit through the leads *BB*. When the measurements have been completed and while the mixture in the capillary *AA* is liquid, the plunger in *D* is raised and the melt is blown out of the capillary into tube *D* by means of a slight pressure of nitrogen on the melt in the tubes *KK*. This procedure is essential as otherwise it is practically impossible to clean the capillary. The pressure between *KK* and *D* is equalized or adjusted by means of stopcock *G*. The cell must of course be cleaned after each series of measurements. This cell was calibrated by means of a 1.0 N solution of potassium chloride, the specific conductance of which was assumed to be 0.1118 at 25°. The solution was made up by weight according to the procedure of Kraus and Parker.¹

The cell constants are given in Table II.

TABLE II
Constants of Cells for Pure Tellurium and Mixtures rich in Tellurium

| Cell No. | R. | Cell Const. |
|----------|------|-------------|
| 1 | 2303 | 257.8 |
| 2 | 6340 | 708.8 |
| 3 | 4435 | 495.8 |

For cells 2 and 3, the lead resistance was determined under working conditions by dipping the electrodes into molten tin and determining the resistance at various temperatures. The leads of cell 1 were the same as those of cell 2 except that the length of platinum was shortened. The corrections for cell 1 were calculated from those of cell 2 assuming the value 0.0036 for the resistance temperature coefficient of platinum. The results are given in Table III.

¹ Kraus and Parker: *J. Am. Chem. Soc.*, 44, 2422 (1922).

TABLE III
Lead Resistance for Cells 1, 2 and 3 at Different Temperatures

| Temp. °C. | Resistance | | |
|-----------|------------|--------|--------|
| | Cell 1 | Cell 2 | Cell 3 |
| 349.6 | 0.3002 | 0.2935 | 0.2900 |
| 369.0 | 0.3029 | 0.2960 | 0.2923 |
| 395.0 | 0.3065 | 0.2985 | 0.2947 |
| 416.0 | 0.3094 | 0.2999 | 0.2959 |
| 429.2 | 0.3113 | 0.3013 | 0.2960 |
| 457.0 | 0.3152 | 0.3044 | 0.2990 |
| 486.0 | 0.3192 | 0.3070 | 0.3018 |

Other Apparatus. The temperature was measured by means of a platinum, platinum-rhodium thermocouple previously calibrated against the melting points of tin, lead, zinc and aluminum and the boiling point of water.

For measuring the resistance of pure tellurium and mixtures of tellurium and sulphur, containing up to 15 at. % of sulphur, a Leeds and Northrup precision bridge was used. For mixtures containing 30 or more at. % of sulphur, a Kohlrausch bridge and telephone were employed. With a 30 at. % mixture, the resistance as measured according to the two methods differed by about one-half percent due to polarization effects which were noticeable in the case of the D.C. method. Mixtures containing more than 30 at. % of sulphur showed marked polarization effects.

Procedure. In the case of mixtures rich in sulphur the desired quantities of sulphur and tellurium were weighed out, ground together in an agate mortar and introduced into the cell (Fig. 3). The cell was then evacuated and filled with nitrogen. The thermostat was brought to a temperature somewhat above the melting point of the mixture, whereupon the cell was introduced into the thermostat. When the mixture was melted, the electrodes were lowered into the fused mass and the mixture was stirred until a constant value of the resistance was reached. The resistance of the melt was then measured at a series of temperatures.

Tellurium-rich mixtures were premelted in a Pyrex tube under an atmosphere of nitrogen at a pressure of approximately two atmospheres. Special precautions were observed to avoid the loss of sulphur. When the mass was melted, it was thoroughly shaken and then cooled rapidly. The product was removed, when cold, and introduced into tube *D* of the conductivity cell (Fig. 4). The cell was evacuated and filled with nitrogen and a slow stream of nitrogen was kept passing through the upper part of the cell through tubes *E* and *F* against a slight pressure of mercury in a trap attached to *F*. When the mixture was melted, the plunger was depressed as described above, forcing the melt into the capillary *AA* of the cell, after which the resistance was measured at a series of temperatures.

In the case of pure tellurium, the metal, which had received an additional distillation in vacuo, was introduced into tube *D* of the cell (Fig. 4) and melted under nitrogen. The manipulation was similar to that described above in the

case of the mixtures rich in tellurium. It was necessary to carry resistance measurements out as rapidly as possible since tellurium reacts slowly with the platinum electrodes at higher temperatures.

Tellurium has a marked tendency to undercool so that it was possible to extend the conductance measurements a considerable distance into the metastable region of the liquid phase. On solidifying, a discontinuous change occurs in the resistance. In series 1, the cell was provided with a compara-

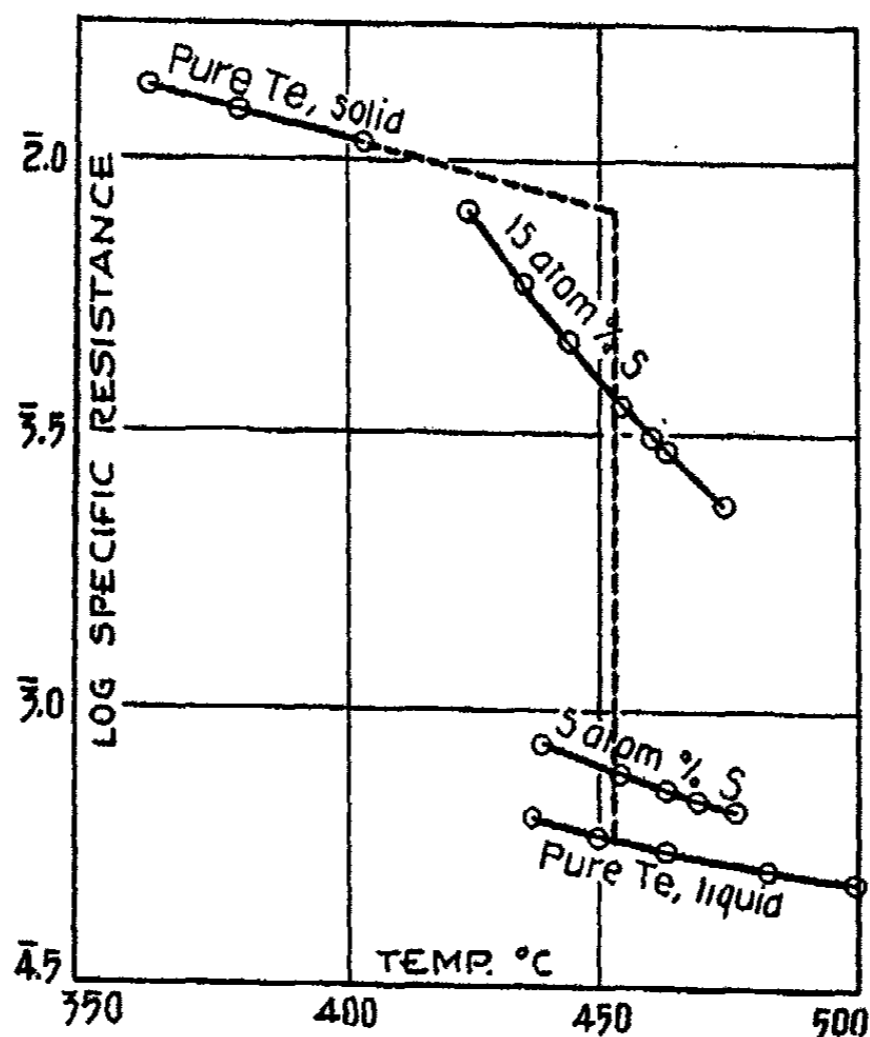


FIG. 5
Resistance of Tellurium and of Sulphur-Tellurium Mixtures

tively large capillary and it was possible to measure the resistance of the solid phase over a considerable temperature range. This was not found possible in the case of cells 2 and 3 which were provided with smaller capillaries, since, owing to contraction which follows solidification, the thread of metal ruptured shortly after solidification occurred.

III. Experimental Results

Cell 1 was used in determining the resistance of pure tellurium in the solid state (Series 1). In this series the values for liquid tellurium are not very precise since the resistance was very low and a small error in the lead resistance caused a relatively large error in the final result. The values for the solid, however, are fairly accurate, since the resistance of this phase is much greater than that of the liquid. More precise data for the conductance of liquid tellurium were obtained in Series 2 in which the resistance of the

capillary was much higher than in Series 1. The results for pure tellurium and for various mixtures of tellurium and sulphur are tabulated below.

TABLE IV

Specific Resistance of Tellurium and of Mixtures of Tellurium and Sulphur
Series 1. Pure Tellurium (Cell 1)

| Temp. | R. | R. (Corr.) | Sp. R. $\times 10^3$ | |
|-------|--------|------------|----------------------|--------|
| 480.5 | 0.4442 | 0.1257 | 0.488 | Liquid |
| 466.0 | 0.4515 | 0.1351 | 0.525 | |
| 457.2 | 0.4575 | 0.1423 | 0.553 | |
| 449.1 | 0.4631 | 0.1490 | 0.579 | |
| 437.0 | 0.4762 | 0.1638 | 0.636 | |
| 431.8 | 0.4825 | 0.1708 | 0.663 | |
| 404.7 | 3.319 | 3.011 | 11.69 | Solid |
| 380.5 | 3.732 | 3.427 | 13.31 | |
| 363.0 | 4.116 | 3.814 | 14.81 | |

Series 2. Pure Tellurium (Cell 2)

| | | | |
|-------|--------|--------|-------|
| 499.9 | 0.6599 | 0.3513 | 0.496 |
| 483.1 | 0.6774 | 0.3705 | 0.523 |
| 463.8 | 0.7045 | 0.3996 | 0.564 |
| 450.9 | 0.7291 | 0.4255 | 0.600 |
| 438.0 | 0.7613 | 0.4590 | 0.648 |

Series 3. 5 At.% Sulphur (Cell 3)

| | | | | |
|-------|--------|--------|-------|--------|
| 464.0 | 0.6619 | 0.3622 | 0.731 | Liquid |
| 477.0 | 0.6341 | 0.3334 | 0.673 | |
| 469.9 | 0.6481 | 0.3479 | 0.702 | |
| 455.0 | 0.6862 | 0.3872 | 0.781 | |
| 440.3 | 0.7392 | 0.4415 | 0.891 | |
| 427.5 | 0.8065 | 0.5099 | 1.028 | |
| 428.0 | 7.115 | 6.818 | 13.75 | Solid |
| 409.5 | 10.31 | 10.02 | 20.21 | |
| 382.0 | 12.06 | 11.77 | 23.74 | |

Series 4. 15 At.% Sulphur (Cell 3)

| | | | |
|-------|-------|-------|-------|
| 445.3 | 2.790 | 2.492 | 5.026 |
| 461.2 | 1.948 | 1.649 | 3.326 |
| 474.8 | 1.537 | 1.236 | 2.493 |
| 464.0 | 1.858 | 1.559 | 3.145 |
| 455.6 | 2.182 | 1.884 | 3.800 |
| 436.5 | 3.455 | 3.158 | 6.370 |
| 425.5 | 4.628 | 4.332 | 8.738 |

TABLE IV (Continued)

| Temp. | R. | R. (Corr.) | Sp. R. $\times 10^3$ |
|---------------------------------------|---------------------|-------------------------|----------------------|
| Series 5. 30 At. % Sulphur (Cell 3) | | | |
| 420.0 | 188.0 | 187.7 | 378.6 |
| 436.0 | 131.0 | 130.7 | 263.6 |
| 457.5 | 75.4 | 75.1 | 151.5 |
| 474.1 | 49.9 | 49.6 | 100.0 |
| 455.0 | 81.7 | 81.4 | 164.2 |
| 444.2 | 104.5 | 105.2 | 212.2 |
| 426.0 | 160.4 | 160.1 | 322.9 |
| 400.0 | 294.3 | 294.0 | 593.0 |
| Series 6. 50 At. % Sulphur (Cell 3) | | | |
| Temp. | R. $\times 10^{-3}$ | Sp. R. $\times 10^{-3}$ | |
| 398.0 | 16.29 | 0.0328 | |
| 421.5 | 10.90 | .0220 | |
| 440.3 | 7.44 | .0156 | |
| 469.2 | 4.01 | .0081 | |
| 455.8 | 5.35 | .0108 | |
| 440.1 | 7.58 | .0151 | |
| 423.0 | 10.81 | .0218 | |
| 416.5 | 12.31 | .0248 | |
| Series 7. 70 At. % Sulphur (Cell 4) | | | |
| Temp. | R. $\times 10^{-3}$ | Sp. R. $\times 10^{-3}$ | |
| 471.6 | 3.72 | 1.08 | |
| 461.6 | 4.44 | 1.29 | |
| 451.3 | 5.28 | 1.53 | |
| 437.8 | 6.67 | 1.94 | |
| 415.1 | 10.06 | 2.92 | |
| 408.2 | 11.45 | 3.33 | |
| 387.0 | 16.76 | 4.87 | |
| Series 8. 75 At. % Sulphur (Cell 5) | | | |
| 429.2 | 31.3 | 19.3 | |
| 448.0 | 21.8 | 13.5 | |
| 426.0 | 32.3 | 19.9 | |
| 399.3 | 54.7 | 33.8 | |
| 375.0 | 88.0 | 54.3 | |
| Series 9. 77.5 At. % Sulphur (Cell 6) | | | |
| 464.1 | 54.8 | 21.9 | |
| 454.9 | 64.9 | 26.0 | |
| 434.1 | 90.7 | 36.3 | |
| 425.5 | 111.0 | 44.4 | |
| 403.9 | 163.0 | 65.2 | |
| 406.1 | 154.0 | 61.6 | |
| 390.1 | 210.0 | 84.0 | |
| 404.1 | 160.0 | 64.0 | |
| Series 10. 80 At. % Sulphur (Cell 7) | | | |
| 456.1 | 200.0 | 83.2 | |
| 450.8 | 221. | 81.9 | |
| 429.0 | 340. | 141.0 | |
| 430.5 | 323. | 134.0 | |
| 418.0 | 421. | 175.0 | |
| 405.0 | 541. | 225.0 | |
| 397.0 | 655. | 272.0 | |
| 399.3 | 600. | 250.0 | |
| Series 11. 85 At. % Sulphur (Cell 8) | | | |
| 394.0 | 2770.0 | 1380.0 | |
| 404.6 | 1530. | 762. | |
| 425.5 | 928. | 462. | |
| 437.5 | 482. | 240. | |
| 444.0 | 409. | 204. | |
| 440.1 | 465. | 232. | |
| 435.2 | 530. | 264. | |
| 428.0 | 692. | 345. | |
| 418.1 | 958. | 477. | |

The results for pure tellurium and mixtures containing 5 and 15 at. % sulphur respectively, are shown graphically in Fig. 5, in which the logarithm of the specific resistance is plotted against the temperature. The corresponding plots for mixtures containing higher percentages of sulphur are similar to those obtained at 5 and 15 at. % except that the curves are steeper and more nearly linear.

From the plots, values of the specific resistance of various mixtures at a temperature of 440° were read off. These values are given in Table V.

TABLE V

Specific Resistance of Mixtures of Sulphur and Tellurium at 440°C

| At. % S. | Sp. R. | At. % S. | Sp. R. |
|----------|------------------------|----------|---------------------|
| 0.0 | 6.410×10^{-4} | 70.0 | 1.870×10^3 |
| 5.0 | 8.910×10^{-4} | 75.0 | 1.592×10^4 |
| 15.0 | 5.741×10^{-3} | 77.5 | 3.365×10^4 |
| 30.0 | 2.390×10^{-1} | 80.0 | 1.145×10^5 |
| 50.0 | 1.571×10 | 85.0 | 2.317×10^5 |

Discussion

As may be seen from an inspection of Fig. 5, the logarithm of the specific resistance varies approximately as a linear function of the temperature for mixtures of tellurium and sulphur as well as for pure tellurium. With increasing sulphur content the specific resistance increases markedly. This is illustrated in Fig. 6, where the logarithm of the specific resistance is plotted as a function of the composition of the mixture. The resistance of a mixture containing 5 at. % of tellurium does not differ greatly from that of pure tellurium while that of a 15 at. % mixture has a resistance approximately ten times that of pure tellurium at 440°. A mixture containing 85 at. % of sulphur, or 5½ atoms of sulphur per atom of tellurium, has a specific resistance 3.6×10^8 times that of pure tellurium. Evidently, with increasing sulphur content, the specific resistance of the mixture increases indefinitely and the equivalent conducting power of the tellurium in the mixture approaches a value of zero.

With pure tellurium, as well as with mixtures containing 5 and 15 at. % sulphur, no indications of polarization were observed. Beginning with 30 at. % of sulphur and at higher sulphur concentrations, polarization effects became marked, indicating the presence of ordinary ions. Evidently the electrons due to metallic tellurium associate themselves with sulphur atoms or molecules when the number of atoms of sulphur becomes comparable with that of tellurium. This is not unexpected since the affinity of sulphur for the electrons is fairly high. Since sulphur is a non-polar substance, as is indicated by its low dielectric constant, the ionization of tellurium diminishes rapidly with increasing sulphur content. Evidently the law governing the ionization of tellurium in these mixtures is similar to that governing the ionization of ordinary electrolytes in solvents of very low dielectric constant.

The metallic properties due to tellurium are evidently lost when the number of sulphur atoms present in the mixture becomes equal to or slightly greater than that of the tellurium atoms. As has been pointed out elsewhere,¹ the metallic properties of a substance are greatly dependent on the mean distance between the metallic atoms or ions. If this distance is increased considerably above that of the normal metallic element or compound, the metallic properties disappear.

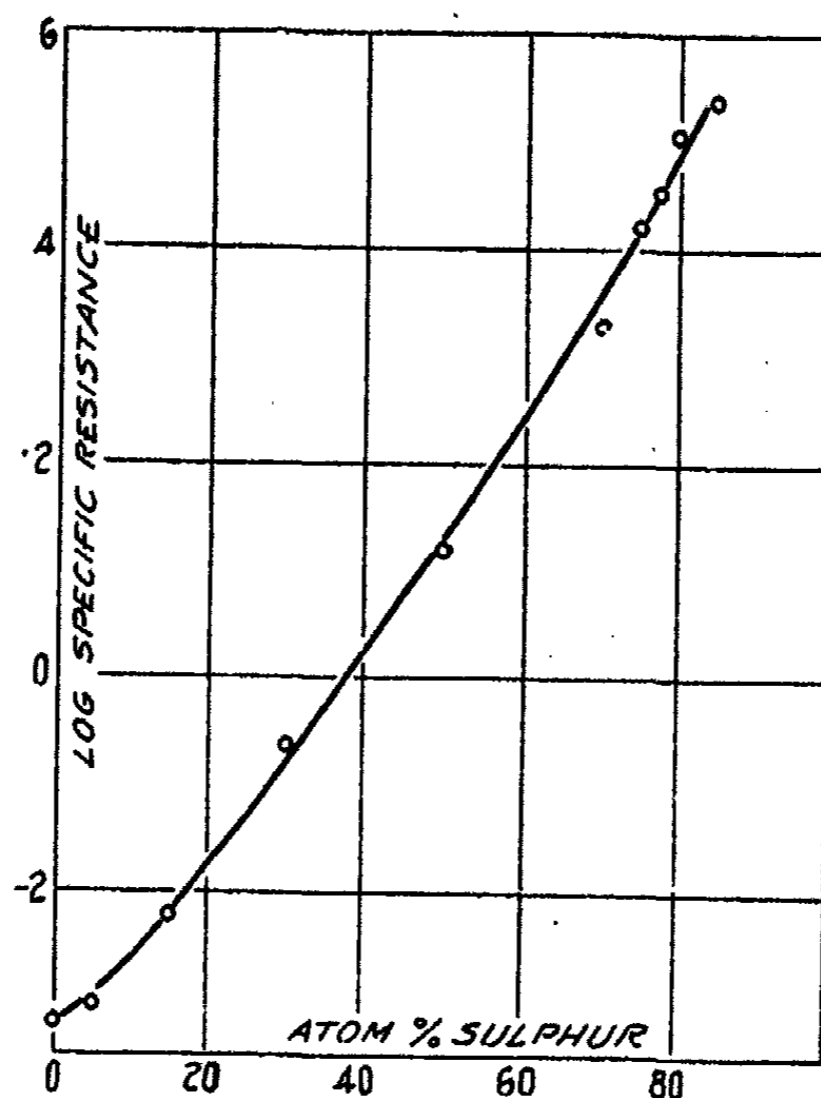


FIG. 6
Resistance of Sulphur-Tellurium Mixtures at 440°.

It is interesting to note that the specific resistance of both solid and liquid tellurium diminishes greatly with increasing temperature and that a large diminution of resistance occurs as the metal passes from the solid to the liquid state. The ratio of the resistances of the element in the two forms is approximately 1 to 15. It may be noted in this connection that the specific volume of solid tellurium is markedly lower than that of the liquid.

Previous data relating to the specific resistance of pure tellurium are very discordant. Matthiessen² gives the value 2.14×10^{-3} for the specific resistance of tellurium at ordinary temperatures while Bridgman³ gives a value 6.45×10^{-3} for a particular specimen at 24°. Beckmann⁴ gives values

¹ Kraus: J. Am. Chem. Soc., 44, 1218 (1922).

² Matthiessen: Pogg. Ann., 103, 428 (1885).

³ Bridgman: Proc. Am. Acad. Arts Sci., 52, 573 (1917).

⁴ Beckmann: Physik. Z., 16, 59 (1915).

ranging from 0.617 to 0.0493 depending on previous treatment. In none of the investigations here cited was the tellurium of known purity. In the present investigation the value found at 263°, the lowest temperature at which measurements were made, is 0.0148 which is much higher than that of Bridgman at ordinary temperatures. Since in the present case, the resistance was found to increase markedly with decreasing temperature, it follows that at ordinary temperatures the specific resistance would probably fall in the neighborhood of the values determined by Beckmann. However, the influence of thermal treatment on specific resistance renders any comparison uncertain if not quite meaningless.

Guntz and Broniewski¹ measured the resistance of a specimen of tellurium through the melting point and found a pronounced maximum for the solid at 50°. Fortsch² found the resistance of solid tellurium decreasing regularly from -79 to 280°. Bridgman, as also Beckmann, found the temperature coefficients varying, depending on previous treatment. Excepting the observations of Guntz and Broniewski, already referred to, which are expressed in arbitrary units, no data are available relative to the specific resistance of liquid tellurium.

Summary

Methods and apparatus are described for determining the specific resistance of liquid mixtures of sulphur and tellurium. The specific resistance of pure tellurium has been measured at higher temperatures for both solid and liquid and that of sulphur-tellurium mixtures, up to 85 at.% of sulphur, has been determined over a considerable temperature range for liquid mixtures.

The specific resistance of the mixtures, as also of pure tellurium, decreases with increasing temperature as an exponential function of the temperature. With increasing sulphur content the specific resistance increases greatly. Evidently the equivalent conducting power of tellurium approaches a value of zero with increasing sulphur content.

The specific resistance of liquid tellurium at its melting point is approximately 1/15 that of solid tellurium at the same temperature. Liquid tellurium is, comparatively, a good conductor; at 500° its specific conductance is about 1/6 that of mercury at ordinary temperatures.

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¹ Guntz and Broniewski: *Compt. rend.*, 147, 1474 (1908).

² Fortsch: *Proc. Iowa Acad. Sci.*, 20, 523 (1919).

THE INFLUENCE OF SALTS ON THE SOLUBILITY OF OTHER SALTS IN NON-AQUEOUS SOLVENTS¹

BY CHARLES A. KRAUS AND RALPH P. SEWARD

I. Introduction.

The mutual solubility relations of salts in aqueous solution are markedly regular and have been the subject of extensive investigation. Apparently, a corresponding study of salt solubilities in non-aqueous solvents has not been made. This problem was originally attacked by Dr. A. B. Stowe² who worked chiefly with acetone. The difficulties inherent in the problem were not completely overcome but his results showed clearly that, in general, the solubility relations parallel those in water, that is, on adding a salt with a common ion, the solubility is depressed while, on adding a salt without a common ion, the solubility is increased.³

The present investigation was undertaken for the purpose of obtaining accurate data with respect to the solubility relations of salts in one or more non-aqueous solvents. Much time was spent in an attempt to obtain results with acetone, but the instability of the solvent rendered the problem extremely difficult so that only a limited series of satisfactory measurements was finally obtained. Isopropyl alcohol was then chosen, since it is stable and may be readily purified. The order of magnitude of the solubility of ordinary salts in this solvent is also exceptionally favorable.

The ultimate aim of this investigation was to gain an insight into the phenomena peculiar to solutions of electrolytes. In order to disentangle the complex phenomena of electrolytic solutions, it is necessary to simplify the problem by working at rather low concentrations. Hitherto, the conductance method has been used almost exclusively in the study of solutions in non-aqueous solvents at low concentrations. Unfortunately, the results of conductance measurements can not be safely interpreted at the present time. The freezing or boiling point method has not thus far been satisfactorily developed in the case of non-aqueous solvents, even at concentrations as high as 0.01 N. It seemed, therefore, that the solubility method might afford the readiest means of investigating the behavior of non-aqueous salt solutions at concentrations as low as 10^{-3} N or lower.

¹ A brief resume of a portion of the results of this paper has appeared in the Transactions of the Faraday Society, 23, 488 (1927).

² Allen B. Stowe: Dissertation, Clark University (1923).

³ Recently King and Partington [Transactions of the Faraday Society, 23, 522 (1927)], have determined the solubility of sodium iodide in ethyl alcohol in the presence of lithium iodide and sodium thiocyanate. Their results are in agreement with our observations in that the solubility of the saturating salt is diminished on the addition of a salt with a common ion. A detailed comparison of their results with ours is not possible because of the great difference in the solubility of the saturating salts.

The mutual solubility effects of salts in aqueous solutions have recently been critically reviewed by A. A. Noyes.¹ He concludes that they are in substantial agreement with the interionic attraction theory of Debye and Hückel.² The results of the present investigation make it possible to test the same theory in the case of solutions in non-aqueous solvents having a value of the dielectric constant in the neighborhood of 20.

II. Materials

Acetone. Commercial acetone was purified by the bisulphite method. Final dehydration was accomplished by treating the solvent with finely powdered boric oxide. This method of dehydration proved very satisfactory but the solvent itself was found to be relatively unstable so that the solubility of the salt changed as the age of the solvent increased.

Isopropyl Alcohol. Commercial petrohol, 91% isopropyl alcohol, was treated with powdered sodium hydroxide. The alcohol layer was distilled and the same process of dehydration repeated until a satisfactory product was obtained. The purified product has a density of 0.785 at 25° and a specific conductance of about 1.5×10^{-7} .

Salts. The best grade of salts were twice recrystallized from water. Sodium chloride was purified by dissolving in hot water and precipitating with hydrogen chloride. All salts were dried before using.

III. Method and Procedure

The method of determining the solubility of the salt consisted in agitating a quantity of the solvent containing a known amount of the added salt and an excess of saturating salt until saturation was reached and then analyzing the solution for the saturating salt. About 5 g. of the saturating salt were finely pulverized in an agate mortar and introduced into a special bottle of cylindrical form, having a length of approximately 38 cm., a diameter of 10 cm., and a capacity of 3 liters. A known weight of the second salt, also finely ground, was introduced into the same bottle and then a known weight of pure solvent (about 2 liters) was introduced from the stock container.

The bottles were provided with narrow necks of about 12 mm. internal diameter with well ground stoppers which were held in position, water tight, by means of special rubber caps. Four bottles were affixed to a spindle which was rotated in a horizontal position under water maintained at a temperature of $25 \pm 0.01^\circ$. Initially, the bottles were rotated for 12 hours at a temperature of 28° - 30° after which the temperature was lowered to 25° and rotated for 6 hours longer. The bottles were then removed from the spindle and set upright without removing from the thermostat and allowed to settle for 3 hours or more. Two samples of 500 cc. or more were then blown from the bottle into glass stoppered Erlenmeyer flasks, the exact amount of solution being

¹ Arthur A. Noyes: J. Am. Chem. Soc., 46, 1098 (1924).

² Debye and Hückel: Physik Z., 24, 185; Debye: 334 (1923); Rec. Trav. chim., 42, 597 (1923).

determined by weight. The solvent was then evaporated, the residue containing the salts was transferred to a beaker and the content of the saturating salt determined analytically.

By far the most convenient salts were combinations of alkali metal halides with nitrates, the halide serving as saturating salt. In this case the halide was determined by precipitation with silver in the usual manner. The concentration of the second salt was known from the amount initially added. In one or two instances, in which the second salt was present up to the saturation point, the amount was determined analytically. At the low concentration of the solutions used, the density did not differ appreciably from that of the pure solvent, hence no correction was made for this factor.

IV. Solubility Effects in Acetone

Only a single series of satisfactory measurements was obtained in the case of this solvent using sodium bromide as saturating salt and sodium nitrate as added salt. The results are given in Table I, concentrations being expressed in millimols per liter.

TABLE I
Solubility of Sodium Bromide in Acetone at 25°
in the presence of Sodium Nitrate

| NaNO ₃ | NaBr(Anal) | NaBr(Mean) | (Σc_i) ^{1/2} × 10 ³ | - $\frac{1}{2}$ log P ₁₀ /P ₁ |
|-------------------|-----------------|------------|---------------------------------------------------|-----------------------------------------------------|
| 0.00 | 0.7674 .7680 | 0.7677 | 39.07 | 0.0000 |
| 0.1371 | 0.7594 .7601 | 0.7597 | 40.68 | .0315 |
| 0.2286 | 0.7436 .7488 | 0.7462 | 41.48 | .0457 |
| 0.6602 | 0.7152 .7105 | 0.7129 | 45.68 | .1102 |

V. Solubility Effects in Isopropyl Alcohol

In this solvent, the solubility of sodium chloride was determined in the presence of sodium nitrate and ammonium nitrate. The solubility of sodium chloride was particularly favorable, being less than 0.5×10^{-3} . With a combination of sodium chloride and sodium nitrate, the analytical procedure worked out very well. In the case of sodium chloride and ammonium nitrate, however, the procedure was less satisfactory as is evidenced by the lack of satisfactory agreement between check determinations. The difficulty was probably due, in part at least, to the volatility of ammonium salts, some loss perhaps occurring in the removal of the alcohol.

The results of the solubility determinations of sodium chloride in the presence of sodium nitrate and ammonium nitrate are given in Tables II and III respectively. In view of the analytical difficulties mentioned in connection with mixtures of sodium chloride and ammonium nitrate, the highest values, rather than the mean, are employed in the subsequent dis-

ussion. These results are somewhat more concordant than are the mean values although the difference would not materially alter the nature of the results. Concentrations are expressed in millimols per liter.

TABLE II
Solubility of Sodium Chloride in Isopropyl Alcohol at 25°
in the presence of Sodium Nitrate

| NaNO ₃ | NaCl(Anal.) | NaCl(Mean) | (ΣCl) ¹ × 10 ³ | -½log P ₁₀ /P ₁ |
|-------------------|-----------------|------------|--------------------------------------|---------------------------------------|
| 0.0000 | 0.4242 .4251 | 0.4246 | 29.14 | 0.0000 |
| 0.0800 | 0.4147 .4172 | 0.4159 | 31.50 | .0292 |
| 0.1672 | 0.4057 .4044 | 0.4050 | 33.84 | .0544 |
| 0.4013 | 0.3812 .3822 | 0.3817 | 39.57 | .1098 |
| 0.5902 | 0.3657 .3594 | 0.3625 | 43.64 | .1412 |
| 0.5984 | 0.3650 .3631 | 0.3640 | 43.87 | .1442 |
| 0.8539 | 0.3502 .3459 | 0.3480 | 49.16 | .1827 |
| 1.3097 | 0.3245 .3239 | 0.3242 | 57.16 | .2340 |
| 1.5574 | 0.3196 .3293 | 0.3244 | 61.32 | .2645 |
| 1.9590 | 0.3081 .3087 | 0.3074 | 67.31 | .2936 |
| 2.8240 | 0.2899 .2908 | 0.2903 | 78.91 | .3501 |

TABLE III
Solubility of Sodium Chloride in Isopropyl Alcohol at 25°
in the presence of Ammonium Nitrate

| NH ₄ NO ₃ | NaCl(Anal.) | NaCl(selected) | (ΣCl) ¹ × 10 ³ | -½log P ₁₀ /P ₁ |
|---------------------------------|-----------------|----------------|--------------------------------------|---------------------------------------|
| 0.0000 | 0.4565 .4541 | 0.455 | 30.16 | 0.0000 |
| 0.0985 | 0.4741 .4811 | 0.481 | 34.12 | .0241 |
| 0.1839 | 0.4838 .5034 | 0.503 | 37.06 | .0436 |
| 0.3537 | 0.5346 .5466 | 0.547 | 42.45 | .0800 |
| 0.6938 | 0.6175 .6096 | 0.617 | 51.20 | .1323 |
| 1.4024 | 0.7342 .6850 | 0.734 | 65.35 | .2027 |

VI. Influence of Water on the Solubility of Sodium Chloride in Isopropyl Alcohol

In the course of this investigation it was soon found that the solubility of various salts was measurably influenced by the presence of traces of water. In order to eliminate any uncertainty due to the presence of water, the influence of water on the solubility of pure sodium chloride, as well as on that of mixtures of sodium chloride and sodium nitrate was investigated.

In Table IV are given values of the solubility of sodium chloride in isopropyl alcohol in the presence of varying amounts of water. The density of the solvent mixture was determined and the concentrations are expressed in millimols of salt per liter of the mixture.

TABLE IV
Solubility of Sodium Chloride in Isopropyl Alcohol at 25°
in the presence of Varying Amounts of Water

| % H ₂ O | NaCl(Anal.) | Density | % H ₂ O | NaCl(Anal.) | Density |
|--------------------|-------------|---------|--------------------|-------------|---------|
| 0.000 | 0.4246 | 0.7849 | 1.39 | 0.8025 | .7885 |
| 0.084 | 0.4399 | .7854 | 2.02 | 1.100 | .7900 |
| 0.815 | 0.6034 | .7868 | 5.88 | 4.138 | .7985 |

To a large quantity of solvent, 2.02% of water was added and the solubility of sodium chloride determined in the presence of varying amounts of sodium nitrate. The results are given in Table V, concentrations being expressed in millimols per liter.

TABLE V
Solubility of Sodium Chloride in Isopropyl Alcohol at 25°
containing 2.02% of Water in the presence of Sodium Nitrate

| NaNO ₃ | NaCl(Anal.) | NaCl(Mean) | (ΣCl) ¹ × 10 ³ | -½log P ₁₀ /P ₁ |
|-------------------|-------------|------------|--------------------------------------|---------------------------------------|
| 0.0000 | 1.1004 | 1.0999 | 46.90 | 0.0000 |
| | 1.0994 | | | |
| 0.1707 | 1.0780 | 1.0796 | 50.00 | .0238 |
| | 1.0813 | | | |
| 0.2697 | 1.0672 | 1.0679 | 51.71 | .0360 |
| | 1.0687 | | | |
| 0.4370 | 1.0460 | 1.0560 | 54.64 | .0576 |
| | 1.0660 | | | |
| 0.8842 | 1.0112 | 1.0139 | 61.60 | .1007 |
| | 1.0167 | | | |
| 1.3597 | 0.9694 | 0.9723 | 68.30 | .1364 |
| | .9752 | | | |
| 2.4412 | 0.9107 | 0.9123 | 81.90 | .2014 |
| | .9140 | | | |
| 6.534 | 0.7985 | 0.7984 | 121.1 | .3424 |
| | .7984 | | | |

VII. Discussion

Concordance of Results. Considering the analytical difficulties, chiefly due to the low solubility of the salts studied, the concordance of the data obtained is fairly satisfactory. This is particularly true of the solubility of sodium chloride in anhydrous and hydrated isopropyl alcohol in the presence of sodium nitrate. With few exceptions, the analytical values agree within less than 1% and the points lie on smooth curves. In Fig. 1 (upper curve) is shown the solubility of sodium chloride in isopropyl alcohol in the presence

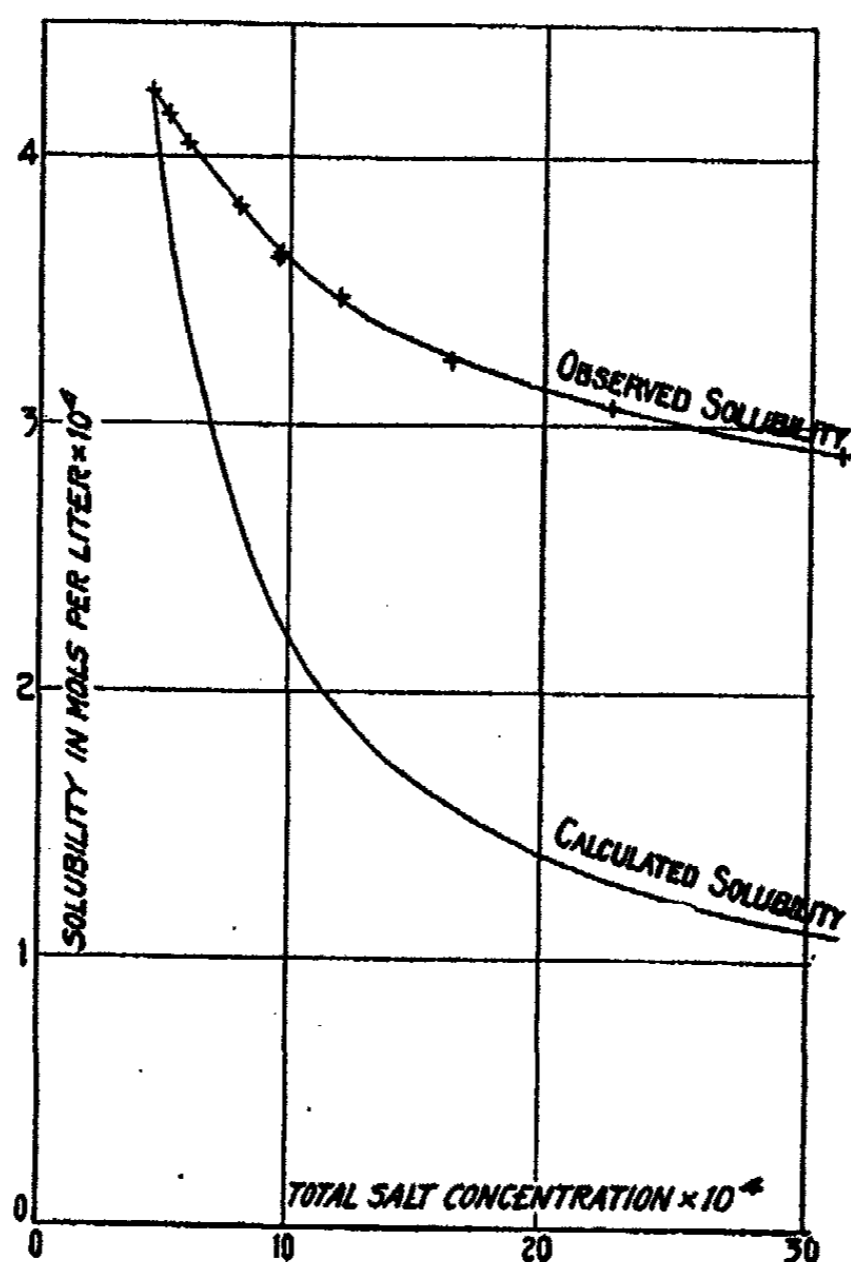


FIG. 1

Comparison of Solubility of Sodium Chloride in Isopropyl Alcohol in the presence of Sodium Nitrate with Value calculated according to Interionic Attraction Theory.

of sodium nitrate as a function of the total salt concentration. As may be seen from the figure, only the 9th point is seriously in error. The two analytical determinations in the case of this point are not in agreement, one of the values being much too high, as is evident from the fact that the solubility as found is greater than at the preceding lower concentration of sodium nitrate. If the high value is rejected, the point conforms well with the curve as drawn. The determinations with sodium chloride in hydrated alcohol, as well as with sodium bromide in acetone, are in good agreement. The

determinations of the solubility of sodium chloride in the presence of ammonium nitrate show considerable variation, probably for the reason already mentioned. However, it is believed that the higher values chosen are not seriously in error.

Comparison with Aqueous Solutions. Roughly, the influence of a uni-univalent salt on the solubility of another salt of the uni-univalent type is much the same in isopropyl alcohol and acetone as it is in water. It is noteworthy that the depression due to an added salt with a common ion is much smaller in isopropyl alcohol and acetone than in water, while the increase in solubility, due to the addition of a salt without a common ion, is much greater in isopropyl alcohol than in water.

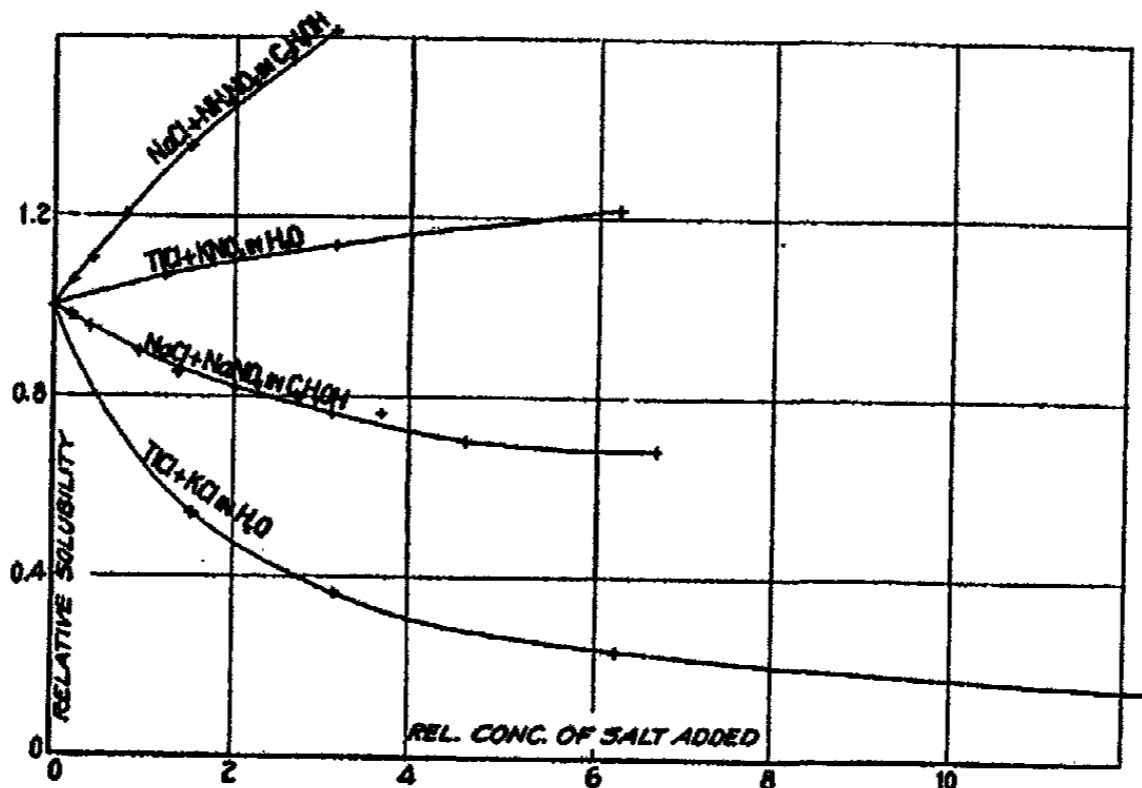


FIG. 2
Relative Solubility Effects in Water and Isopropyl Alcohol compared.

In order to compare the solubility effects, in the present case, with similar effects as observed in aqueous solutions, it is necessary to reduce the concentrations to a common unit. This is conveniently done by dividing the observed values of the solubility, as well as the concentration of the added salt, by the solubility of the saturating salt in the pure solvent. The relative concentrations so obtained thus represent the concentration of a given constituent in terms of the concentration of the saturating salt in the pure solvent. For the purpose of comparison, the relative solubilities and relative concentrations of added salt have been calculated for solutions of thallos chloride in water in the presence of potassium chloride and of potassium nitrate¹ and for sodium chloride in isopropyl alcohol in the presence of sodium nitrate and of ammonium nitrate. The relation between relative solubilities and relative concentrations of added salt is shown graphically in Fig. 2. Some of the values as read from the smooth curves at round relative concentrations are given in Table VI.

¹ Bray and Winninghof: J. Am. Chem. Soc., 33, 1670 (1911).

TABLE VI
Comparison of Solubility Effects in Isopropyl Alcohol and Water
Relative Concentrations

| C added Salt | 0.2 | 0.5 | 1.0 | 2.0 | 3.0 |
|---------------------------------------------------------------------------------|------|------|------|------|------|
| S (TlCl in H ₂ O + KCl) | 0.90 | 0.78 | 0.65 | 0.47 | 0.41 |
| S (NaCl in C ₃ H ₇ OH + NaNO ₃) | 0.98 | 0.94 | 0.90 | 0.82 | 0.77 |
| S (TlCl in H ₂ O + KNO ₃) | 1.01 | 1.03 | 1.06 | 1.10 | 1.13 |
| S (NaCl in C ₃ H ₇ OH + NH ₄ NO ₃) | 1.05 | 1.13 | 1.25 | 1.44 | 1.60 |

As may be seen from Fig. 2, or from Table VI, the solubility of thallos chloride in water, on the addition of potassium chloride, is depressed much more than is that of sodium chloride in isopropyl alcohol on addition of sodium nitrate. For example, on the addition of a second salt, corresponding to 0.2 of the concentration of the saturating salt in the pure solvent, the solubility of thallos chloride is depressed 10% while in isopropyl alcohol the solubility of sodium chloride is depressed only 2%. On the addition of a salt of concentration equal to that of the original salt in pure water, the solubility in the case of thallos chloride is depressed 35% while in isopropyl alcohol the solubility of sodium chloride is depressed only 10%. This means that on adding 16.07 millimols of potassium chloride ($S_0 = 16.07 \times 10^{-3}$) to a solution of thallos chloride in water, the solubility is depressed 35% while on the addition of 0.4246 millimols of sodium nitrate ($S_0 = 0.42 \times 10^{-3}$) to sodium chloride in isopropyl alcohol, the solubility is depressed only 10%. Roughly, therefore, the depressing effect, of a uni-univalent salt on the solubility of a second uni-univalent salt with a common ion is about three and a half times as great in water as it is in isopropyl alcohol. To obtain the same relative depression in isopropyl alcohol as in water, the relative concentration of added salt must be six times as great as in water.

The increased solubility of a uni-univalent salt on addition of a uni-univalent salt without a common ion is much greater in isopropyl alcohol than it is in water. This may be seen from the upper curves of Fig. 2 as well as from Table VI. For example, at a concentration of the added salt corresponding to the relative value 0.2, the solubility of thallos chloride in the presence of potassium nitrate is increased 1%, while that of sodium chloride in the presence of ammonium nitrate in isopropyl alcohol is increased approximately 5%. For a relative concentration of 1.0, the increase of solubility is 6% and 25% respectively in water and isopropyl alcohol. In round numbers, the increase of solubility of a uni-univalent salt in isopropyl alcohol on addition of a second salt without a common ion is about four times as great as it is for a corresponding pair of salts in water. Expressed in other terms, to obtain the same relative increase of solubility in water as in isopropyl alcohol, the relative concentration of added salt in water must be six times that in the alcohol.

The Influence of Water. The effect of water on the solubility of salts in non-aqueous solvents is of considerable significance since, in the interpretation of solubility data, it is necessary to know to what extent water may have

a disturbing influence. The addition of water to isopropyl alcohol results in a marked increase in the solubility of sodium chloride. This is evident from Table V or Fig. 3. Thus, the addition of 2% of water, or 0.886 mols per liter, raises the solubility from 0.4246×10^{-3} to 1.10×10^{-3} mols per liter. The lower curve in Fig. 3 shows that the solubility increases more rapidly than the concentration of the added water. The logarithm of the solubility

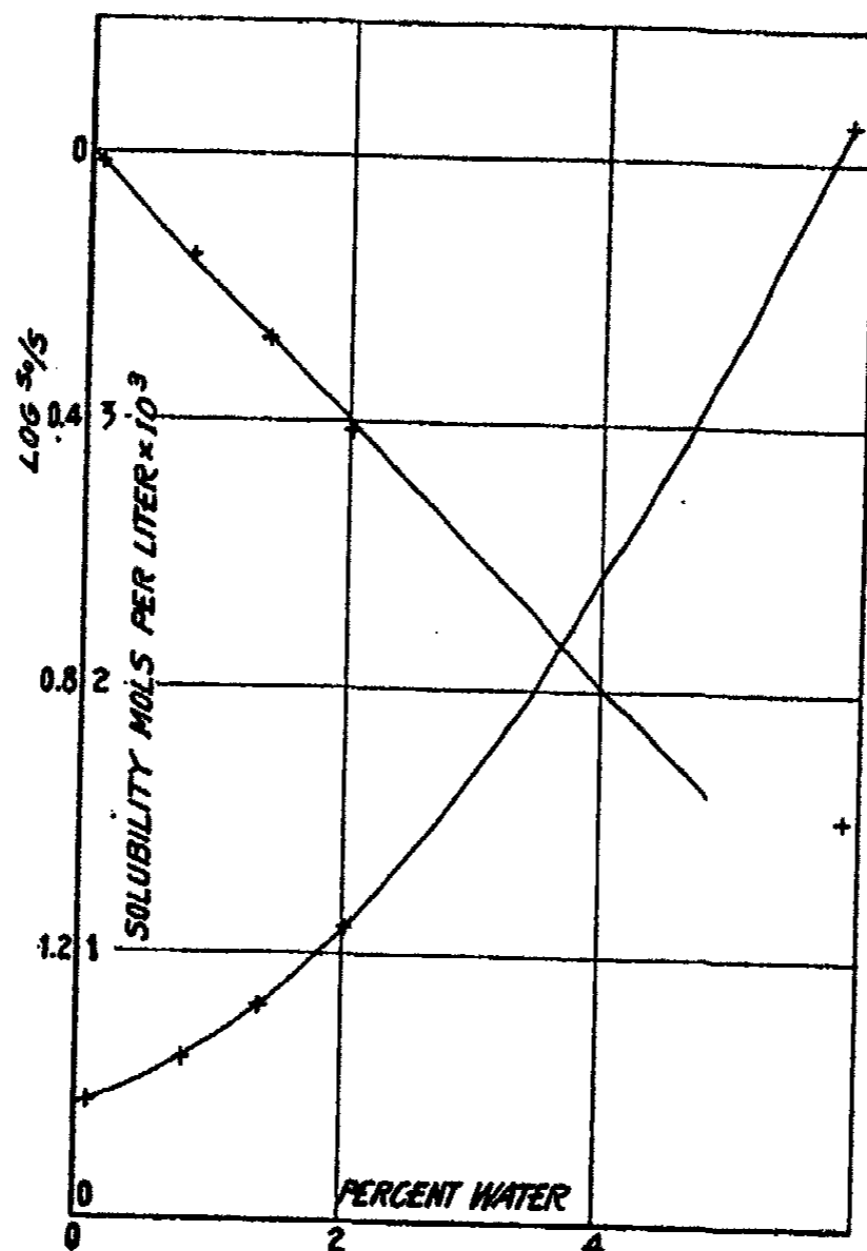


FIG. 3
Showing how the Solubility of Sodium Chloride in Isopropyl Alcohol is influenced by addition of Water.

increases approximately as a linear function of the concentration of water except for the most concentrated solution, as may be seen from the upper curve of Fig. 3. We might interpret this by saying that the thermodynamic potential of the salt in solution is diminished on the addition of water and, if the thermodynamic potential varies as the logarithm of the concentration, then the thermodynamic potential of the salt varies approximately as a linear function of the water concentration. Such an interpretation, however, has no physical significance for only unhydrated salt, either as ions or ion pairs, can be in immediate equilibrium with the pure solid phase. What fraction of the salt is present in the unsolvated condition, we have no means of knowing, but it is probably very small. On the other hand, we have good reason for

believing that the addition of water leads to a disturbance of the solvate equilibrium with the formation of hydrated ions and ion pairs. The formation of new molecular species, on addition of water, raises the solubility. Since we have no knowledge of the fraction of salt present in an unsolvated condition, the interpretation of the thermodynamic potentials, or activities, in terms of stoichiometric concentrations leads to purely fictitious results in the physical sense.

If we assume hydration of the salt to occur according to the equation:



and if the law of mass action is applicable, we obtain for the solubility of the salt the expression:

$$(1) \quad S = S_0 + \frac{S_0 C_{H_2O}^n}{K}$$

where S is the solubility of the salt in the presence of water, S_0 is its solubility in the pure solvent, C_{H_2O} is the concentration of water (mols per liter), K is the equilibrium constant of reaction (a), and n is the number of molecules of water associated with one molecule of salt. C_{H_2O} may be assumed equal to the total concentration of water since only a small fraction of it is associated with the salt. For sodium chloride in the presence of water in isopropyl alcohol, we obtain the values $K = 0.47$ and $n = 1.58$. The concentrations as calculated by means of equation (1), using these constants, do not deviate greatly from the observed values with the exception of the point at the lowest concentration which may well be in error owing to the small solubility change and the possible presence of traces of water. The value $n = 1.58$ may be considered as the mean hydration of the salt. The actual phenomena involved are doubtless more complex than has been assumed and we can place no great weight on the result. Nevertheless it is of interest to note that the value obtained for the hydration of the salt is reasonable as to order of magnitude.

While the addition of 2% of water to isopropyl alcohol increases the solubility of sodium chloride to approximately two and one-half times its value in the pure solvent, the relative solubility effect, on addition of sodium nitrate, differs but little from that in the pure solvent. In Fig. 2, the curve, passing through points indicated by crosses, represents the relative solubility of sodium chloride in pure isopropyl alcohol in the presence of sodium nitrate. If the corresponding curve is calculated for the hydrated alcohol, it is found to rise only a little above that for the pure solvent. It must be concluded, therefore, that, although the order of magnitude of the solubility effects is much increased on addition of water, the relative solubility effects remain substantially unchanged.

The Interionic Attraction Theory. It is of interest to compare the solubility effects observed with the requirements of the interionic attraction theory of Debye and Hückel. As already mentioned, A. A. Noyes has made

a careful study of the solubility effects in water from this point of view and has concluded that the results are in substantial agreement with this theory. A corresponding examination of the results presented in this investigation indicates that these are not in agreement with the interionic attraction theory. For purposes of comparison, Noyes' method has been adopted. As Noyes has shown, according to the theory, the following equation should hold for uni-univalent salts:

$$(2) \quad -\frac{1}{2} \log \frac{P_{10}}{P_1} = \beta[(\Sigma C_i)^{\frac{1}{2}} + (2C_0)^{\frac{1}{2}}].$$

In this equation P_{10} is the product of the ion concentrations of the saturating salt in the pure solvent and P_1 the same product for the salt in the mixture, assuming complete ionization. β is a constant involving the temperature and the dielectric constant of the solvent, ΣC_i is the total concentration of ions, positive and negative, in the solution and is therefore equal to twice the total salt concentration and C_0 is the concentration of the saturating salt in the pure solvent. Obviously, for two salts with a common ion, $P_{10} = C_0$ and $P_1 = C_a(C_a + C_b)$, where C_a is the concentration of the saturating salt in the mixture and C_b the concentration of the added salt. In the case of two salts without a common ion $P_1 = C_a^2$. In water, the constant β has the value 0.357 at 25°. Assuming the dielectric constants¹ of acetone and isopropyl alcohol to be 22 and 20 respectively, we find for β in these solvents the values:

$$\beta(\text{acetone}) = 2.24, \beta(\text{alcohol}) = 2.79.$$

In Fig. 4 are plotted values of $-\frac{1}{2} \log P_{10}/P_1$ against those of $(\Sigma C_i)^{\frac{1}{2}}$. According to the interionic attraction theory, this plot should be linear and the slope should correspond to the value of β for the solvent in question. In Fig. 4 the straight lines, as drawn, correspond to the theoretical curves for isopropyl alcohol and acetone. It will be seen from the figure that the experimental points lie far below the theoretical straight lines and that, moreover, the plots are distinctly curved even up to the lowest concentration of added salt. The divergence of the curve for sodium chloride in the presence of sodium nitrate is markedly greater than that for the same salt in the presence of ammonium nitrate. The divergence in the case of sodium bromide in the presence of sodium nitrate in acetone is markedly greater than in that of sodium chloride in isopropyl alcohol. How great the divergence is between observation and theory, is illustrated in Fig. 1, in which are plotted the actual and calculated values of the solubility of sodium chloride in isopropyl alcohol in the presence of sodium nitrate. Solubilities are plotted as ordinates and total salt concentrations as abscissas. The upper curve represents the observed values; the lower curve calculated values according to equation (2),

¹ A satisfactory value for the dielectric constant of isopropyl alcohol does not appear in the literature. The value adopted is probably not greatly in error, as appears on comparison with the value of this constant for related alcohols.

assuming for the dielectric constant of isopropyl alcohol the value 20. In the case of salts without a common ion, the divergence is equally striking.

The divergence of the experimental results from those required according to the interionic attraction theory bears no apparent relation to the dielectric constant. In order to bring the observed values in the more dilute solutions into conformity with the theory it would be necessary to assume for the dielectric constant the value 5.3 for acetone with sodium bromide and sodium

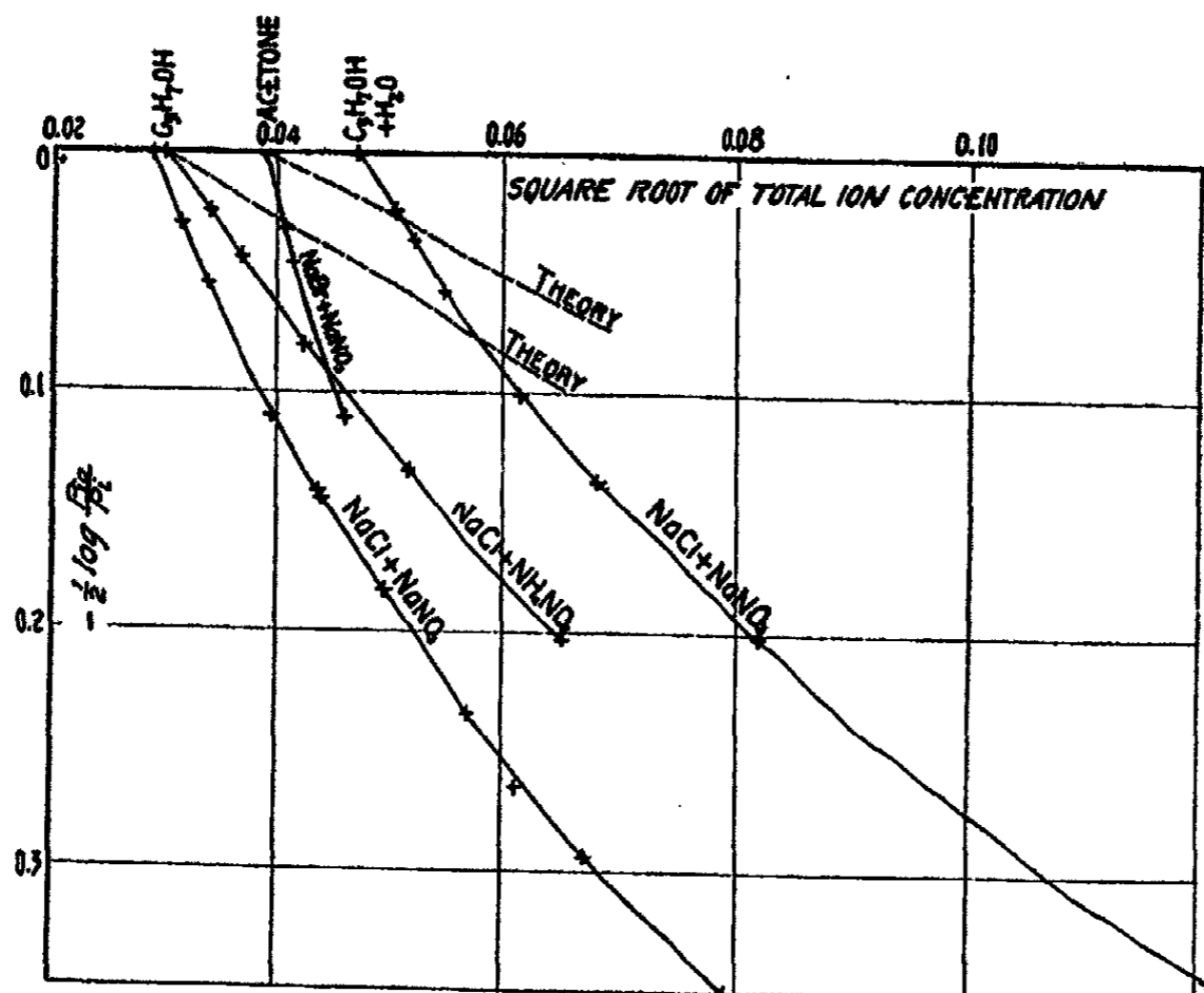


FIG. 4

Comparison of Solubility Effects in Acetone and Isopropyl Alcohol with the Interionic Attraction Theory.

nitrate; 7.2 for isopropyl alcohol with sodium chloride and sodium nitrate, and 11.4 with sodium chloride and ammonium nitrate, and 9.7 for the hydrated alcohol with sodium chloride and sodium nitrate.

The values thus calculated for the dielectric constant would appear to preclude the possibility of accounting for the present discrepancies on the basis of a change in the dielectric constant due to the added salts. In all these cases the total salt concentration is of the order of 10^{-3} or less. Evidently, the dielectric constant is not the determining factor in these solutions. Thus, the dielectric constant of acetone, if anything, is greater than that of isopropyl alcohol, yet the deviation for acetone is much greater than for isopropyl alcohol. In the latter solvent, the deviations are much greater for the combination sodium chloride-sodium nitrate than for sodium bromide-ammonium nitrate, while for the hydrated alcohol, the deviations are

markedly smaller than for the pure solvent. While the addition of 2% of water would doubtless increase the dielectric constant slightly, there is no reason for believing that this would be sufficient to account for the observed results.

It seems evident that the mutual solubility effects of salts are characteristic not only of the salt but also of the solvent and it is reasonable to look for an explanation of the phenomena in a specific interaction between the solvent molecules and the ions or ion pairs of the salt.

The discrepancies between the values observed and those predicted according to the interionic attraction theory are so great that it is difficult to see how they can be reconciled without introducing new concepts. While the theory has met with marked success in the case of aqueous solutions it seems doubtful that it will meet with equal success in the case of solutions in non-aqueous solvents. If the solubility effects as observed in water may be looked upon as a confirmation of the theory, then the corresponding effects observed in the case of non-aqueous solutions must weigh equally against it.

It would seem that in electrolytic solutions in solvents of lower dielectric constant it will be necessary to assume that the process of ionization is incomplete. Solutions of salts in non-aqueous solvents, generally, behave much as do aqueous solutions of weak acids and bases. The ultimate solution of the problem is, perhaps, to be looked for in a combination of the interionic attraction theory with some other concept that takes into account the mechanism of the ionization process. The theory takes account of the mutual forces acting between the ions, once they exist as such, but it tells us nothing with regard to the process by which these ions come into existence.

With decreasing value of the dielectric constant the force acting between a pair of ions increases, and it is not unreasonable to suppose that ion pairs may approach each other sufficiently closely to act as a unit from the kinetic point of view. The process of ionization would then consist in supplying to such an ion pair a sufficient amount of energy to separate the ions against the attractive force of their charges. This would naturally depend upon the nearness of approach of the ions and the spatial configuration of their electronic systems, as well as the dielectric constant of the solvent medium. There are not a few facts that are in agreement with this point of view. In a given solvent, ionization depends mainly on the effective ion diameters which in some cases may correspond to ion diameters as determined for pure salts and in others as determined for solvated ions in solution. The formation of solvated ions involves specific factors relating to both the ions and to the solvent molecules. According to this view, the affinity of the negative ion for an electron has nothing to do with the tendency of the salt to ionize; for this does not affect the energy required to separate a pair of ions. The affinity of a positive ion for an electron may, however, be directly involved.

It should be pointed out that, qualitatively, the results of the present investigation are in agreement with the view that electrolytes are incompletely ionized in solvents having dielectric constants of intermediate value. The low depression of the solubility of a salt on the addition of another salt with

a common ion and the great increase of solubility on the addition of a salt without a common ion lend support to the view that unionized molecules, that is, ion pairs, exist in these solutions. It may be foreseen that in the case of solvents having still lower dielectric constants than those here investigated, the mutual solubility effects may become relatively very large for salt pairs without a common ion, even at low concentrations of the added salt.

Summary

The influence of uni-univalent salts on the solubility of other uni-univalent salts in acetone and in isopropyl alcohol has been investigated. These include sodium bromide in the presence of sodium nitrate in acetone, sodium chloride in the presence of sodium nitrate and ammonium nitrate in isopropyl alcohol and sodium chloride in the presence of sodium nitrate in hydrated isopropyl alcohol.

The solubility effects in these solvents resemble those in water, that is, the solubility of a given salt is depressed on addition of a second salt with a common ion and is increased on addition of a second salt without a common ion. The solubility depression in these solvents is about one-fourth that in water while the increase, on addition of a salt without a common ion, is about four times as great as in water.

The results obtained have been examined from the standpoint of the interionic attraction theory of Debye and Hückel. The observed effects are much smaller than predicted according to the theory.

It is suggested that, in order to account for the observed effects, the interionic attraction theory will have to be supplemented by other assumptions which take into account the specific interactions between the ions and the solvent as well as between the ions themselves.

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THE INFLUENCE OF THE INTENSITY OF INCIDENT LIGHT ON THE VELOCITY OF SOME PHOTOCHEMICAL REACTIONS

BY B. K. MUKERJI AND N. R. DHAR

Very few photochemical reactions have been investigated from this point of view. Draper¹ in 1843 first established that in the reaction between hydrogen and chlorine the chemical change was proportional to the intensity of the light. During recent years various investigators have been at work to settle this problem which is still unsolved.

Another reaction which has been taken up in recent years from this point of view is the photochemical oxidation of potassium oxalate by iodine. This reaction was first investigated by Dhar² who has definitely established that the temperature coefficient of the reaction decreases with the increase in the intensity of the light. We have now studied quantitatively the influence of the change of intensity of light on the rate of this as well as the following fourteen reactions.

1. Chromic acid and oxalic acid in presence of manganous sulphate and sulphuric acid.
2. Sodium citrate and iodine.
3. Ammonium oxalate and iodine.
4. Sodium malate and iodine.
5. Sodium nitrite and iodine in presence of sodium acetate.
6. Sodium formate and iodine in presence of sodium acetate.
7. Sodium-potassium tartrate and bromine in presence of sodium acetate.
8. Ferrous sulphate and iodine.
9. Bleaching of dicyanin.
10. Oxidation of iodoform in benzene as solvent.
11. Sodium formate and mercuric chloride in presence of sodium acetate.
12. Ammonium oxalate and mercuric chloride in presence of eosin as sensitiser.
13. Oxidation of quinine by chromic acid in presence of sulphuric acid.
14. Oxidation of malic acid by potassium permanganate in presence of sulphuric acid.

¹ Phil. Mag., 23, 401 (1843).

² J. Chem. Soc., 111, 707 (1917); 123, 1856 (1923).

Experimental

The experimental arrangement adopted for these investigations is as follows:—

A thermostat was maintained at a constant temperature and water from it was circulated by means of an automatic syphon inside a hollow double-walled rectangular jacket made of copper, the ends of which could be closed by means of shuttered screens. Inside the hollow space of this jacket was placed a closely-fitting rectangular glass cell with parallel ends which served as the vessel in which the reaction took place.

A thermometer with graduations up to 0.1° was always kept suspended with its bulb dipping inside the reacting system—so that the temperature at which the reaction took place could be controlled within $\pm 0.1^{\circ}$.

A 1000-watt gas-filled tungsten-filament lamp operated at 4.6 amperes was used as the source of light in these experiments. To check the constancy of the current consumed, an ammeter was connected in series with the lamp. Owing to the intense heating effect produced by the lamp an electric radiator had to be constantly used at the back of the lamp. The lamp and the radiator were enclosed in a box made of thick wood with asbestos cardboard lining inside. In order to get the maximum intensity and a parallel beam of light a combination of two big condenser glass lenses was placed in position between the source of light and the reaction vessel.

To isolate any particular region of wave-lengths a combination of two light filters out of a set of gelatin film "Wallace M and S" filters manufactured by the Central Scientific Company was used.

A screened iris diaphragm was placed between the light filters and the reaction vessel in such a way that all light excepting that passing through the aperture was prevented from falling on the reacting mixture. The change in the intensity of the incident light was effected by varying the size of the aperture and it was taken to be directly proportional to the area of the aperture through which the light finally passed before illuminating the reaction vessel.

The changes in the reactions studied were observed by withdrawing some of the reacting mixtures at noted intervals of time and subjecting it to spectrophotometric measurements or suitable titrations.

In all the experiments the superimposed thermal reactions were deducted from the total reaction carried on in light in order to obtain the effect due only to light.

I (a). Potassium oxalate and iodine.

$K_2C_2O_4$ — N/2.52; I_2 — N/100; KI — N/30.

No light filter was used.

Temperature $20^{\circ}C$.

| (i) Diameter of the aperture = 2.0 cm. | | | | | |
|------------------------------------------|----------------------------------------------------------|--------------------------|-----------------|----------------------------------------------------------|--------------------------|
| Time in minutes | Sodium thio-sulphate* per 3 c.c. of the reacting mixture | k_4 (**semi-molecular) | Time in minutes | Sodium thio-sulphate* per 3 c.c. of the reacting mixture | k_4 (**semi-molecular) |
| 0 | 4.85 c.c. | — | 30 | 4.2 c.c. | 0.0102 |
| 15 | 4.5 | 0.0108 | 50 | 3.85 | 0.00960 |
| Mean = | | | | | 0.0102 |
| (ii) Diameter of the aperture = 1.2 cm. | | | | | |
| 0 | 4.85 c.c. | — | 52 | 4.25 c.c. | 0.00542 |
| 25 | 4.55 | 0.00560 | 105 | 3.65 | 0.00556 |
| Mean = | | | | | 0.00543 |
| (iii) Diameter of the aperture = 1.0 cm. | | | | | |
| 0 | 4.85 c.c. | — | 56 | 4.25 c.c. | 0.00500 |
| 32 | 4.5 | 0.00506 | 84 | 3.95 | 0.00512 |
| Mean = | | | | | 0.00506 |

* The concentrations of iodine per 3 c.c. of the reacting mixture being directly proportional to the respective thiosulphate titre, logarithmic values of the latter have been taken directly in the above computations.

** The formula for the semi-molecular velocity constant is $k_4 = (2/t) (\sqrt{a} - \sqrt{a-x})$, where the symbols have the usual significance.

The oxidation of potassium oxalate by iodine proceeds in the darkness at a rate which is negligible in comparison with the velocity obtained photochemically. Hence, in considering the final result the values obtained in (i), (ii) and (iii) were directly utilised.

Result:—

| | |
|--------------------------------|-----------------|
| Diameter of aperture No. (i) | = 2.0 cm. |
| Area of the aperture | = 3.142 sq. cm. |
| Diameter of aperture No. (ii) | = 1.2 cm. |
| Area of the aperture | = 1.31 sq. cm. |
| Diameter of aperture No. (iii) | = 1.0 cm. |
| Area of the aperture | = 0.786 sq. cm. |

| I. | II. If directly proportional to change in intensity | III. If proportional to the square root of the change of intensity |
|---------------------------------------------------------------------------------------|--------------------------------------------------------------|--------------------------------------------------------------------------------|
| $\frac{\text{Velocity (i)}}{\text{Velocity (ii)}} = \frac{0.0102}{0.00553} = 1.84$ | $\frac{3.142}{1.131} = 2.78$ | $\sqrt{2.78} = 1.77$ |
| $\frac{\text{Velocity (i)}}{\text{Velocity (iii)}} = \frac{0.0102}{0.00506} = 2.02$ | $\frac{3.142}{0.786} = 4.00$ | $\sqrt{4.00} = 2.00$ |
| $\frac{\text{Velocity (ii)}}{\text{Velocity (iii)}} = \frac{0.00553}{0.00506} = 1.09$ | $\frac{1.131}{0.786} = 1.44$ | $\sqrt{1.44} = 1.17$ |

From the above results it is apparent that the change in the velocities of the reaction is proportional to the square root of the change in the intensities of the incident radiation because the values found experimentally in column I agree with the theoretical results obtained in column III within the limits of experimental error.

This experiment was repeated by using light-filters, apertures of different dimensions as well as different concentrations of the reactants.

The following are the experimental results:—

(b) Potassium oxalate and iodine.

$K_2C_2O_4$ — N/2.95; I_2 — N/113.6; KI — N/29.35.

Filters 8 and 3 ($\lambda_{5000-4450 \text{ \AA}}$).

Mean $\lambda = 4725 \text{ \AA}$.

Temp. 30°C .

(i) Diameter of aperture = 3.55 cm.

| Time in minutes | Sodium thio-sulphate per 5 c.c. of the mixture | k_1 | Time in minutes | Sodium thio-sulphate per 5 c.c. of the mixture | k_1 |
|-----------------|------------------------------------------------|--------|-----------------|------------------------------------------------|--------|
| 0 | 7.13 c.c. | — | 30 | 6.2 c.c. | 0.0121 |
| 13 | 6.7 | 0.0126 | 60 | 5.25 | .0126 |
| Mean = | | | | | 0.0124 |

(ii) Diameter of the aperture = 3.09 cm.

| Time in minutes | Sodium thio-sulphate per 5 c.c. of the mixture | k_1 | Time in minutes | Sodium thio-sulphate per 5 c.c. of the mixture | k_1 |
|-----------------|------------------------------------------------|--------|-----------------|------------------------------------------------|--------|
| 0 | 7.13 c.c. | — | 40 | 5.9 c.c. | 0.0121 |
| 22 | 6.45 | 0.0120 | 60 | 5.5 | .0110 |
| Mean = | | | | | 0.0117 |

(iii) Diameter of the aperture = 2.65 cm.

| Time in minutes | Sodium thio-sulphate per 5 c.c. of the mixture | k_1 | Time in minutes | Sodium thio-sulphate per 5 c.c. of the mixture | k_1 |
|-----------------|------------------------------------------------|--------|-----------------|------------------------------------------------|--------|
| 0 | 7.13 c.c. | — | 50 | 5.7 c.c. | 0.0113 |
| 26 | 6.4 | 0.0108 | 68 | 5.25 | .0111 |
| Mean = | | | | | 0.0111 |

Result:—

Area of aperture (i) = 9.893 sq. cm.

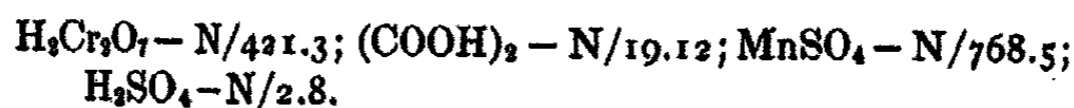
Area of aperture (ii) = 7.495 sq. cm.

Area of aperture (iii) = 5.513 sq. cm.

| I. | | II. If directly proportional to change in intensity | | III. If proportional to the square root of the change of intensity | |
|------------------------------------------------------------------------------------|--|--------------------------------------------------------|--|-----------------------------------------------------------------------|--|
| $\frac{\text{Velocity (i)}}{\text{Velocity (ii)}} = \frac{0.0124}{.0117} = 1.06$ | | $\frac{9.893}{7.495} = 1.32$ | | $\sqrt{1.32} = 1.15$ | |
| $\frac{\text{Velocity (i)}}{\text{Velocity (iii)}} = \frac{0.0124}{.0111} = 1.22$ | | $\frac{9.893}{5.513} = 1.79$ | | $\sqrt{1.79} = 1.34$ | |
| $\frac{\text{Velocity (ii)}}{\text{Velocity (iii)}} = \frac{0.0117}{.0111} = 1.05$ | | $\frac{7.495}{5.513} = 1.36$ | | $\sqrt{1.36} = 1.17$ | |

Here, too we find that the change in the velocities of the reaction in light of $\lambda 4725 \text{ \AA}$ is proportional to the square root of the changes in the intensities of the incident radiation.

II. Chromic acid and oxalic acid in presence of manganese sulphate and sulphuric acid.



Filters 8 and 3 ($\lambda_{5000} - 4450 \text{ \AA}$).

Mean $\lambda = 4725 \text{ \AA}$.

Temperature = 31°C .

(i) Diameter of aperture = 3.55 cm.

| Time in minutes | Sodium thio-sulphate per 5 c.c. of the reacting mixture | k_0 (zero-molecular) | Time in minutes | Sodium thio-sulphate per 5 c.c. of the reacting mixture | k_0 (zero-molecular) |
|-----------------|---------------------------------------------------------|------------------------|-----------------|---------------------------------------------------------|------------------------|
| 0 | 6.0 c.c. | — | 13 | 2.9 c.c. | 0.239 |
| 3 | 5.2 | 0.267 | 17 | 2.0 | .235 |
| 8 | 3.9 | .263 | Mean = | | 0.251 |

(ii) Diameter of aperture = 3.09 cm.

| Time in minutes | Sodium thio-sulphate per 5 c.c. of the reacting mixture | k_0 (zero-molecular) | Time in minutes | Sodium thio-sulphate per 5 c.c. of the reacting mixture | k_0 (zero-molecular) |
|-----------------|---------------------------------------------------------|------------------------|-----------------|---------------------------------------------------------|------------------------|
| 0 | 6.0 c.c. | — | 18 | 2.1 c.c. | 0.217 |
| 5 | 4.95 | 0.210 | 23 | 1.5 | .200 |
| 12 | 3.4 | .216 | Mean = | | 0.211 |

(iii) Diameter of aperture = 2.65 cm.

| Time in minutes | Sodium thio-sulphate per 5 c.c. of the reacting mixture | k_0 (zero-molecular) | Time in minutes | Sodium thio-sulphate per 5 c.c. of the reacting mixture | k_0 (zero-molecular) |
|-----------------|---------------------------------------------------------|------------------------|-----------------|---------------------------------------------------------|------------------------|
| 0 | 6.0 c.c. | — | 19 | 2.2 c.c. | 0.200 |
| 8 | 4.4 | 0.200 | 25 | 0.9 | .204 |
| 13 | 3.4 | .200 | Mean = | | 0.201 |

* The formula used for the zero-molecular velocity coefficient = $k_0 = x/t$, where "x" is the change in concentration of chromic acid in "t" minutes.

The value of " k_0 " in the darkness = 0.131

Pure light effect in (i) = 0.120

Pure light effect in (ii) = 0.080

Pure light effect in (iii) = 0.0700

Result:—

| | I. | II. If directly proportional to change in intensity | III. If proportional to the square root of the change of intensity |
|----------------------------------------------------------------------------------|----|--------------------------------------------------------|-----------------------------------------------------------------------|
| $\frac{\text{Velocity (i)}}{\text{Velocity (ii)}} = \frac{0.120}{.080} = 1.50$ | | 1.32 | 1.15 |
| $\frac{\text{Velocity (i)}}{\text{Velocity (iii)}} = \frac{0.120}{.070} = 1.71$ | | 1.79 | 1.34 |
| $\frac{\text{Velocity (ii)}}{\text{Velocity (iii)}} = \frac{0.080}{.070} = 1.14$ | | 1.36 | 1.17 |

The values obtained in column I agree more closely to the values given in column II than to those in column III. Hence, the velocities of this reaction are directly proportional to the intensities of the incident radiation.

III. Sodium citrate and iodine.

Sodium citrate — N/11.52; Iodine — N/100; Potassium iodide — N/27.

No light filter was used.

Temperature 32°C.

(i) Diameter of the aperture = 3.55 cm.

| Time in minutes | Sodium thio-sulphate per 5 c.c. of the reacting mixture | k_1 | Time in minutes | Sodium thio-sulphate per 5 c.c. of the reacting mixture | k_1 |
|-----------------|---------------------------------------------------------|---------|-----------------|---------------------------------------------------------|---------|
| 0 | 8.6 c.c. | — | 56 | 7.5 c.c. | 0.00700 |
| 19 | 8.2 | 0.00726 | 76 | 7.1 | 0.00700 |
| 38 | 7.8 | 0.00732 | | Mean = | 0.00715 |

(ii) Diameter of the aperture = 3.09 cm.

| Time in minutes | Sodium thio-sulphate per 5 c.c. of the reacting mixture | k_1 | Time in minutes | Sodium thio-sulphate per 5 c.c. of the reacting mixture | k_1 |
|-----------------|---------------------------------------------------------|---------|-----------------|---------------------------------------------------------|---------|
| 0 | 8.6 c.c. | — | 80 | 7.25 c.c. | 0.00600 |
| 20 | 8.25 | 0.00600 | 100 | 6.95 | 0.00614 |
| 50 | 7.7 | 0.00632 | | Mean = | 0.00612 |

(iii) Diameter of the aperture = 2.65 cm.

| Time in minutes | Sodium thio-sulphate per 5 c.c. of the reacting mixture | k_1 | Time in minutes | Sodium thio-sulphate per 5 c.c. of the reacting mixture | k_1 |
|-----------------|---------------------------------------------------------|---------|-----------------|---------------------------------------------------------|---------|
| 0 | 8.6 c.c. | — | 75 | 7.45 c.c. | 0.00541 |
| 28 | 8.15 | 0.00550 | 100 | 7.1 | 0.00556 |
| 50 | 7.8 | 0.00556 | | Mean = | 0.00551 |

The corresponding value for " k_1 " in the darkness = 0.00312.

Therefore, the effect of pure light in (i) = 0.00403

Therefore, the effect of pure light in (ii) = 0.00300

Therefore the effect of pure light in (iii) = 0.00239

Result:—

| | I. | II. If directly proportional to incident intensity | III. If proportional to the square root of the incident intensity |
|--------------------------------------------|------|-------------------------------------------------------|----------------------------------------------------------------------|
| Velocity (i) = $\frac{0.00403}{0.00300}$ | 1.34 | 1.32 | 1.15 |
| Velocity (ii) = $\frac{0.00403}{0.00239}$ | 1.69 | 1.79 | 1.34 |
| Velocity (iii) = $\frac{0.00300}{0.00239}$ | 1.25 | 1.36 | 1.17 |

That is, the velocities of this reaction are directly proportional to the intensities of the incident light.

IV. Ammonium oxalate and iodine.

Ammonium oxalate = N/6.57; Iodine — N/100; Potassium iodide — N/2.7.

Filters 8 and 3 ($\lambda_{5000} - 4450 \text{ \AA.}$).Mean $\lambda = 4725 \text{ \AA.}$ Temp. 215°C.

(i) Diameter of the aperture = 3.55 cm.

| Time in minutes | Thio used per 5 c.c. of the reacting mixture | $1/2.3 \times k_1$ (unimolecular) | Time in minutes | Thio used per 5 c.c. of the reacting mixture | $1/2.3 \times k_1$ (unimolecular) |
|-----------------|----------------------------------------------|-----------------------------------|-----------------|----------------------------------------------|-----------------------------------|
| 0 | 4.95 c.c. | — | 30 | 3.7 c.c. | 0.00421 |
| 10 | 4.5 | 0.00414 | 37 | 3.45 | 0.00424 |
| 22 | 4.0 | 0.00420 | | Mean = | 0.00420 |

(ii) Diameter of the aperture = 3.09 cm.

| | | | | | |
|----|-----------|---------|------|----------|---------|
| 0 | 4.95 c.c. | — | 32 | 3.8 c.c. | 0.00359 |
| 13 | 4.45 | 0.00356 | 38.5 | 3.5 | 0.00361 |
| 25 | 4.05 | 0.00350 | | Mean = | 0.00357 |

(iii) Diameter of the aperture = 2.65 cm.

| | | | | | |
|----|-----------|---------|----|-----------|---------|
| 0 | 4.95 c.c. | — | 42 | 3.65 c.c. | 0.00315 |
| 15 | 4.45 | 0.00308 | 60 | 3.2 | 0.00316 |
| 30 | 4.0 | 0.00308 | | Mean = | 0.00312 |

In this case, the velocity in the darkness is negligibly small in comparison with the values obtained in the above experiments. Hence, the elimination of the superimposed thermal effect is not necessary in obtaining the following results:—

Result:—

| | I. | II. If directly proportional to the change of intensity | III. If proportional to the square root of the change of intensity |
|----------------------------------------------------------------------------------------|----|------------------------------------------------------------|-----------------------------------------------------------------------|
| $\frac{\text{Velocity (i)}}{\text{Velocity (ii)}} = \frac{0.00420}{0.00357} = 1.176$ | | 1.32 | 1.15 |
| $\frac{\text{Velocity (i)}}{\text{Velocity (iii)}} = \frac{0.00420}{0.00312} = 1.346$ | | 1.79 | 1.34 |
| $\frac{\text{Velocity (ii)}}{\text{Velocity (iii)}} = \frac{0.00357}{0.00312} = 1.144$ | | 1.36 | 1.17 |

There is more concordance within the limits of experimental error between the values shown in columns I and III than between those in columns I and II.

Therefore the velocities of this reaction vary proportionally to the square root of the changes in the intensities of the incident light.

V. Sodium malate and iodine.

Sodium malate - N/6.78; Iodine - N/111.6; Potassium iodide - N/33.87.

No light filter was used.

Temp. 30°C.

(i) Diameter of aperture = 3.55 cm.

| Time in minutes | Thio used per 5 c.c. of the reacting mixture | k_4 (semi-molecular) | Time in minutes | Thio used per 5 c.c. of the reacting mixture | k_4 (semi-molecular) |
|-----------------|----------------------------------------------|------------------------|-----------------|----------------------------------------------|------------------------|
| 0 | 5.95 c.c. | — | 45 | 3.1 c.c. | 0.0206 |
| 15 | 4.2 | 0.0221 | 62 | 2.65 | 0.0193 |
| 33 | 3.5 | 0.0214 | | Mean = | 0.0209 |

(ii) Diameter of aperture = 3.09 cm.

| | | | | | |
|----|-----------|--------|----|-----------|--------|
| 0 | 4.95 c.c. | — | 55 | 3.05 c.c. | 0.0174 |
| 20 | 4.2 | 0.0176 | 72 | 2.6 | 0.0170 |
| 40 | 3.55 | 0.0171 | | Mean = | 0.0173 |

(iii) Diameter of the aperture = 2.65 cm.

| | | | | | |
|----|-----------|--------|----|-----------|--------|
| 0 | 4.95 c.c. | — | 66 | 2.95 c.c. | 0.0154 |
| 22 | 4.2 | 0.0160 | 84 | 2.5 | 0.0154 |
| 44 | 3.55 | 0.0155 | | Mean = | 0.0156 |

k_4 in the dark = 0.00203

Therefore,

The effect of pure light in (i) = 0.0189

The effect of pure light in (ii) = 0.0153

The effect of pure light in (iii) = 0.0136

Result:—

| I. | II. If directly proportional to intensity | III. If proportional to the square root of intensity |
|-------------------------------------------------------------------------------------|----------------------------------------------|---------------------------------------------------------|
| $\frac{\text{Velocity (i)}}{\text{Velocity (ii)}} = \frac{0.0189}{0.0153} = 1.24$ | 1.32 | 1.15 |
| $\frac{\text{Velocity (i)}}{\text{Velocity (iii)}} = \frac{0.0189}{0.0136} = 1.39$ | 1.79 | 1.34 |
| $\frac{\text{Velocity (ii)}}{\text{Velocity (iii)}} = \frac{0.0153}{0.0136} = 1.13$ | 1.36 | 1.17 |

The velocities of this reaction are thus found to be directly proportional to the intensities of the incident light.

VI. Sodium nitrate and iodine.

Sodium nitrite - 0.56 N; Sodium acetate - N/7.29;

Iodine - N/29.73; Potassium iodide - N/8.115.

Filters 8 and 3 ($\lambda_{5000} - 4450\text{\AA}$).Mean $\lambda = 4725\text{\AA}$

Temp. 33°C.

(i) Diameter of the aperture = 3.55 cm.

| Time in minutes | Thio used per 5 c.c. of the reacting mixture | k_1 (semi-molecular) | Time in minutes | Thio used per 5 c.c. of the reacting mixture | k_1 (semi-molecular) |
|-----------------|----------------------------------------------|------------------------|-----------------|----------------------------------------------|------------------------|
| 0 | 8.9 c.c. | — | 50 | 6.75 c.c. | 0.0154 |
| 10 | 8.45 | 0.0170 | 70 | 5.95 | 0.0155 |
| 30 | 7.6 | 0.0151 | | Mean = | 0.0158 |

(ii) Diameter of the aperture = 3.09 cm.

| Time in minutes | Thio used per 5 c.c. of the reacting mixture | k_1 (semi-molecular) | Time in minutes | Thio used per 5 c.c. of the reacting mixture | k_1 (semi-molecular) |
|-----------------|----------------------------------------------|------------------------|-----------------|----------------------------------------------|------------------------|
| 0 | 8.9 c.c. | — | 60 | 6.65 c.c. | 0.0123 |
| 15 | 8.3 | 0.0137 | 75 | 6.15 | 0.0134 |
| 35 | 7.55 | 0.0135 | | Mean = | 0.0132 |

(iii) Diameter of the aperture = 2.65 cm.

| Time in minutes | Thio used per 5 c.c. of the reacting mixture | k_1 (semi-molecular) | Time in minutes | Thio used per 5 c.c. of the reacting mixture | k_1 (semi-molecular) |
|-----------------|----------------------------------------------|------------------------|-----------------|----------------------------------------------|------------------------|
| 0 | 8.9 c.c. | — | 60 | 6.9 c.c. | 0.0120 |
| 20 | 8.2 | 0.0120 | 80 | 6.3 | 0.0119 |
| 40 | 7.5 | 0.0123 | | Mean = | 0.0121 |

The value of " k_1 " in the darkness = 0.0052. Therefore,

The pure photochemical effect in (i) = 0.0106

The pure photochemical effect in (ii) = .0080

The pure photochemical effect in (iii) = .0069

| I. | | II. | III. |
|------------------------------------------------------------------------------------|--|--------------------------------------------------------|-----------------------------------------------------|
| | | If directly proportional to the intensity of the light | If proportional to the square root of the intensity |
| $\frac{\text{Velocity (i)}}{\text{Velocity (ii)}} = \frac{0.0106}{.0080} = 1.33$ | | 1.32 | 1.15 |
| $\frac{\text{Velocity (i)}}{\text{Velocity (iii)}} = \frac{0.0106}{.0069} = 1.55$ | | 1.79 | 1.34 |
| $\frac{\text{Velocity (ii)}}{\text{Velocity (iii)}} = \frac{0.0080}{.0069} = 1.16$ | | 1.36 | 1.17 |

It is difficult to decide definitely whether the reaction is directly proportional to the intensity or is proportional to the square root. On the whole, from the experimental results it appears that the velocity of the reaction is proportional to the square root of the intensity.

VII. Sodium formate and iodine

Sodium formate - N/6.42; Iodine - N/118.92; Potassium iodide - N/32.46; Sodium acetate - N/7.29.
 Filters 8 and 3. ($\lambda_{5000} - 4450 \text{ \AA}$).
 Mean $\lambda = 4725 \text{ \AA}$.
 Temp. 30°C .

(i) Diameter of aperture = 3.55 cm.

| Time in minutes | Thio used per 5 c.c. of the mixture | k_t (semi-molecular) | Time in minutes | Thio used per 5 c.c. of the mixture | k_t (semi-molecular) |
|-----------------|-------------------------------------|------------------------|-----------------|-------------------------------------|------------------------|
| 0 | 3.65 c.c. | — | 24 | 1.1 c.c. | 0.0718 |
| 8 | 2.6 | 0.0746 | 30 | 0.7 | 0.0716 |
| 15 | 1.9 | 0.0710 | | Mean = | 0.0723 |

(ii) Diameter of the aperture = 3.09 cm.

| | | | | | |
|----|-----------|--------|----|-----------|--------|
| 0 | 3.65 c.c. | — | 22 | 1.55 c.c. | 0.0605 |
| 8 | 2.8 | 0.0600 | 30 | 1.0 | 0.0607 |
| 15 | 2.1 | 0.0616 | | Mean = | 0.0607 |

(iii) Diameter of the aperture = 2.65 cm.

| | | | | | |
|------|-----------|--------|------|----------|--------|
| 0 | 3.65 c.c. | — | 24.5 | 1.5 c.c. | 0.0557 |
| 9 | 2.8 | 0.0528 | 30 | 1.2 | 0.0544 |
| 15.5 | 2.24 | 0.0530 | 38 | 0.8 | 0.0535 |
| | | | | Mean = | 0.0539 |

The value of " k_t " in darkness = 0.0457

Therefore,

The effect of pure light in (i) = 0.0266

The effect of pure light in (ii) = 0.0150

The effect of pure light in (iii) = 0.0082

Result:—

| I. | II. If proportional to the squares of intensities of the incident light | III. If directly proportional to the intensities |
|-------------------------------------------------------------------------------------|----------------------------------------------------------------------------|-----------------------------------------------------|
| $\frac{\text{Velocity (i)}}{\text{Velocity (ii)}} = \frac{0.0266}{0.0150} = 1.77$ | 1.74 | 1.33 |
| $\frac{\text{Velocity (i)}}{\text{Velocity (iii)}} = \frac{0.0266}{0.0082} = 3.24$ | 3.204 | 1.79 |
| $\frac{\text{Velocity (ii)}}{\text{Velocity (iii)}} = \frac{0.0150}{0.0082} = 1.83$ | 1.85 | 1.36 |

From the above it is clear that the velocities of this reaction change directly as the square of the intensities of the incident light.

VIII. Sodium-potassium tartrate and bromine in presence of sodium acetate.

Rochelle salt - N/18.345; Sodium acetate - N/7.29; Bromine
- N/210.9.

Filters 8 and 3 ($\lambda_{5000} - 4450 \text{ \AA}$).

Mean $\lambda = 4725 \text{ \AA}$.

Temp. 30°C .

(i) Diameter of the aperture = 3.55 cm.

| Time in minutes | Thio used per 3 c.c. of the reacting mixture | $1/2.3 \times k_1$ (unimolecular) | Time in minutes | Thio used per 3 c.c. of the reacting mixture | $1/2.3 \times k_1$ (unimolecular) |
|-----------------|----------------------------------------------|-----------------------------------|-----------------|----------------------------------------------|-----------------------------------|
| 0* | 8.0 c.c. | — | 21 | 2.5 c.c. | 0.0241 |
| 13 | 3.95 | 0.0236 | 38 | 0.9 | .0249 |
| | | | | | Mean = 0.0242 |

(ii) Diameter of the aperture = 3.09 cm.

| | | | | | |
|----|----------|--------|----|-----------|---------------|
| 0 | 7.8 c.c. | — | 23 | 3.05 c.c. | 0.0177 |
| 14 | 4.45 | 0.0174 | 50 | 1.0 | .0178 |
| | | | | | Mean = 0.0176 |

(ii) Diameter of the aperture = 2.65 cm.

| | | | | | |
|----|-----------|--------|----|----------|---------------|
| 0 | 7.15 c.c. | — | 32 | 2.5 c.c. | 0.0143 |
| 12 | 4.8 | 0.0144 | 80 | 0.5 | .0144 |
| | | | | | Mean = 0.0144 |

* As there is an instantaneous reaction between sodium acetate and bromine the readings were commenced some time after the mixing up of the reactants. The sodium acetate is added in order to avoid the difficulty that the hydrogen ion formed in the reaction greatly retards the change.

The corresponding " k_1 " in the darkness = 0.0101

Therefore,

Pure light effected in (i) = 0.0141

Pure light effected in (ii) = .0075

Pure light effected in (iii) = .0043

Result:—

| I. | | II. | III. |
|----------------|-------------------------------|--------------------------------------------------|---------------------------------------------|
| | | If proportional to the square of the intensities | If directly proportional to the intensities |
| Velocity (i) | $\frac{0.0141}{.0075} = 1.89$ | 1.74 | 1.32 |
| Velocity (ii) | $\frac{0.0141}{.0043} = 3.28$ | 3.204 | 1.79 |
| Velocity (iii) | $\frac{0.0075}{.0043} = 1.74$ | 1.85 | 1.36 |

The velocities of this reaction vary, too, as the square of the intensities of the incident light energy.

IX. Ferrous sulphate and iodine.

$\text{FeSO}_4 - \text{N}/12; \text{I}_2 - \text{N}/125; \text{KI} - \text{N}/37.5.$

No filter was used.

Temp. $19.5^\circ\text{C}.$

(i) Diameter of the aperture = 2.0 cm.

| Time in minutes | Thio for 3 c.c. of the reacting mixture | k_t (semimolecular) | Time in minutes | Thio for 3 c.c. of the reacting mixture | k_t (semimolecular) |
|-----------------|-----------------------------------------|-----------------------|-----------------|-----------------------------------------|-----------------------|
| 0 | 41. c.c. | — | 36 | 2.8 c.c. | 0.0196 |
| 12 | 3.65 | 0.0190 | 54 | 2.25 | .0194 |
| 25 | 3.2 | .0190 | 66 | 1.85 | .0202 |
| | | | | | Mean = 0.0194 |

(ii) Diameter of the aperture = 1.2 cm.

| Time in minutes | Thio for 3 c.c. of the reacting mixture | k_t (semimolecular) | Time in minutes | Thio for 3 c.c. of the reacting mixture | k_t (semimolecular) |
|-----------------|-----------------------------------------|-----------------------|-----------------|-----------------------------------------|-----------------------|
| 0 | 4.1 c.c. | — | 60 | 2.9 c.c. | 0.0107 |
| 15.5 | 3.75 | 0.0123 | 80 | 2.55 | .0107 |
| 40 | 3.25 | .0111 | 100 | 2.25 | .0105 |
| | | | | | Mean = 0.0111 |

(iii) Diameter of the aperture = 1.0 cm.

| Time in minutes | Thio for 3 c.c. of the reacting mixture | k_t (semimolecular) | Time in minutes | Thio for 3 c.c. of the reacting mixture | k_t (semimolecular) |
|-----------------|-----------------------------------------|-----------------------|-----------------|-----------------------------------------|-----------------------|
| 0 | 4.1 c.c. | — | 85 | 2.75 c.c. | 0.00861 |
| 15 | 3.8 | 0.0101 | 105 | 2.5 | .00844 |
| 65 | 2.8 | .0108 | | | |
| | | | | | Mean = 0.00949 |

The corresponding " k_t " in the dark = 0.00569
Therefore,

The effect of light alone in (i) = 0.0137

The effect of light alone in (ii) = 0.00541

The effect of light alone in (iii) = 0.00380

Result:—

| I. | II. If directly proportional to the intensity | III. If proportional to the square root of the intensity of the incident light |
|-------------------------------------------------------------|--------------------------------------------------|-----------------------------------------------------------------------------------|
| $\frac{\text{Velocity (i)}}{\text{Velocity (ii)}} = 2.53$ | 2.778 | 1.77 |
| $\frac{\text{Velocity (i)}}{\text{Velocity (iii)}} = 3.61$ | 4.00 | 2.00 |
| $\frac{\text{Velocity (ii)}}{\text{Velocity (iii)}} = 1.42$ | 1.44 | 1.17 |

It appears from the above that the reaction between ferrous sulphate and iodine is directly proportional to the intensity of the incident light.

X. Bleaching of dicyanin.

Initial strength of dicyanin - $M/27140$.Filters 4 and 7 ($\lambda_5^{\circ}50 - 5450 \text{ \AA}$).Mean $\lambda = 5650 \text{ \AA}$.

Zero correction = 0.48 on the density scale.

Thickness of observation cell = 0.385 cm.

Temp. 31°C .

Diameter of the aperture = 3.55 cm.

| Time in minutes | Reading on the density scale | Corrected reading on the density scale | Extinction coefficient. | $1/2.3 \times k_1$ |
|-----------------|------------------------------|----------------------------------------|-------------------------|--------------------|
| 0 | 1.02 | 0.54 | 1.4026 | _____ |
| 22 | 0.95 | .47 | 1.2208 | 0.002740 |
| 52 | 0.88 | .40 | 1.0389 | .002507 |
| 100 | .76 | .28 | 0.7273 | .002852 |
| 130 | .72 | .24 | .6234 | .002709 |
| 176 | .65 | .17 | .4416 | .002847 |
| | | | | Mean = 0.002731 |

(ii) Diameter of the aperture = 3.09 cm.

| | | | | |
|-----|------|------|--------|-----------------|
| 0 | 1.02 | 0.54 | 1.4026 | _____ |
| 30 | 0.95 | .47 | 1.2208 | 0.002010 |
| 85 | .84 | .36 | 0.9351 | .002071 |
| 120 | .78 | .30 | .7792 | .002127 |
| 164 | .72 | .24 | .6234 | .002147 |
| | | | | Mean = 0.001790 |

(iii) Diameter of the aperture = 2.65 cm.

| | | | | |
|-----|------|------|--------|-----------------|
| 0 | 1.02 | 0.54 | 1.4026 | _____ |
| 40 | 0.94 | .46 | 1.1948 | 0.001741 |
| 100 | .84 | .36 | 0.9351 | .001761 |
| 125 | .80 | .32 | .8311 | .001818 |
| 155 | .76 | .28 | .7273 | .001840 |
| | | | | Mean = 0.001790 |

"k₁" in the dark = 0.000902

Therefore,

The pure photochemical reaction in (i) = 0.001829

The pure photochemical reaction in (ii) = .001187

The pure photochemical reaction in (iii) = .000888

Result:—

| I. | | II. | III. |
|----------------|-----------------------------------|-------------------------------------------|-----------------------------------------------------|
| | | If directly proportional to the intensity | If proportional to the square root of the intensity |
| Velocity (i) | $\frac{0.001829}{.001187} = 1.54$ | 1.32 | 1.15 |
| Velocity (ii) | $\frac{0.001829}{.000888} = 2.06$ | 1.79 | 1.34 |
| Velocity (iii) | $\frac{0.001187}{.000888} = 1.34$ | 1.36 | 1.17 |

The rate of this change is directly proportional to the intensity of the incident light.

XI. Oxidation of iodoform in benzene as solvent.
M/40 Iodoform in benzene.

For estimating the iodine concentrations, 3 c.c. of the mixture was withdrawn at intervals and run into a large excess of cold water and removed to darkness where it was kept for 30 minutes before titration with standardised sodium thiosulphate—the same amount of dilute starch solution being used every time as indicator.

No light filter was used.
Temp. 23°C.

(i) Diameter of the aperture = 1.6 cm.

| Time in minutes | Thio used per 3 c.c. solution | k_0 = (zero-molecular) | Time in minutes | Thio used per 3 c.c. solution | k_0 = (zero-molecular) |
|-----------------|-------------------------------|--------------------------|-----------------|-------------------------------|--------------------------|
| 0* | 3.15 c.c. | — | 14 | 4.6 c.c. | 0.104 |
| 6 | 3.75 | 0.100 | 25 | 5.9 | .110 |
| | | | | | Mean = 0.105 |

(ii) Diameter of the aperture = 1.4 cm.

| Time in minutes | Thio used per 3 c.c. solution | k_0 = (zero-molecular) | Time in minutes | Thio used per 3 c.c. solution | k_0 = (zero-molecular) |
|-----------------|-------------------------------|--------------------------|-----------------|-------------------------------|--------------------------|
| 0 | 3.2 c.c. | — | 18 | 4.6 c.c. | 0.0800 |
| 7 | 3.75 | 0.0800 | 28 | 5.5 | .0821 |
| | | | | | Mean = 0.0807 |

(iii) Diameter of the aperture = 1.0 cm.

| Time in minutes | Thio used per 3 c.c. solution | k_0 = (zero-molecular) | Time in minutes | Thio used per 3 c.c. solution | k_0 = (zero-molecular) |
|-----------------|-------------------------------|--------------------------|-----------------|-------------------------------|--------------------------|
| 0 | 3.25 c.c. | — | 17 | 3.9 c.c. | 0.0382 |
| 9 | 3.6 | 0.0390 | 27 | 4.3 | .0390 |
| | | | | | Mean = 0.0387 |

* The zero time in the above experiments was noted some minutes after the light was turned on.

Result:—

| I. | II. If directly proportional to change in intensity | III. If proportional to the square root of the change in intensity |
|-------------------------------------------------------------------------------------|--------------------------------------------------------|-----------------------------------------------------------------------|
| $\frac{\text{Velocity (i)}}{\text{Velocity (ii)}} = \frac{0.015}{.0807} = 1.301$ | 1.304 | 1.142 |
| $\frac{\text{Velocity (i)}}{\text{Velocity (iii)}} = \frac{0.105}{.0387} = 2.713$ | 2.560 | 1.600 |
| $\frac{\text{Velocity (ii)}}{\text{Velocity (iii)}} = \frac{0.0807}{.0387} = 2.085$ | 1.963 | 1.401 |

Thus the velocities of this reaction change proportionally to the intensity of the incident light.

XII. Sodium formate and mercuric chloride in presence of sodium acetate.

Sodium formate — 0.898N; Mercuric chloride — M/15; Sodium acetate — 0.2813 gm. in 20 c.c.

The change in the concentration of mercuric chloride was determined by drawing out 3 c.c. of the reacting mixture at noted intervals, running it into an excess of potassium iodide solution of known strength and titrating back the remaining potassium iodide with a standardised solution of mercuric chloride.

No light filter was used.

Temp. 20°C.

(i) Diameter of the aperture = 2.0 cm.

| Time in minutes | Gram-mol. of mercuric chloride per 3 c.c. of the solution | $1/2.3 \times k_1$ | Time in minutes | Gram-mol. of mercuric chloride per 3 c.c. of the solution | $1/2.3 \times k_1$ |
|-----------------|-----------------------------------------------------------|--------------------|-----------------|-----------------------------------------------------------|--------------------|
| 0 | 0.0001823 | — | 102 | 0.0001265 | 0.00156 |
| 44 | .0001555 | 0.00157 | 180 | .00009486 | .001568 |
| Mean = 0.00157 | | | | | |

(ii) Diameter of the aperture = 1.2 cm.

| Time in minutes | Gram-mol. of mercuric chloride per 3 c.c. of the solution | $1/2.3 \times k_1$ | Time in minutes | Gram-mol. of mercuric chloride per 3 c.c. of the solution | $1/2.3 \times k_1$ |
|-----------------|-----------------------------------------------------------|--------------------|-----------------|-----------------------------------------------------------|--------------------|
| 0 | 0.0001820 | — | 110 | 0.0001414 | 0.00104 |
| 50 | .0001618 | 0.00104 | 139 | .0001302 | .00105 |
| Mean = 0.00104 | | | | | |

(iii) Diameter of the aperture = 1.0 cm.

| Time in minutes | Gram-mol. of mercuric chloride per 3 c.c. of the solution | $1/2.3 \times k_1$ | Time in minutes | Gram-mol. of mercuric chloride per 3 c.c. of the solution | $1/2.3 \times k_1$ |
|-----------------|-----------------------------------------------------------|--------------------|-----------------|-----------------------------------------------------------|--------------------|
| 0 | 0.0001823 | — | 120 | 0.0001476 | 0.000864 |
| 47 | .0001678 | 0.000866 | 180 | .0001322 | .000875 |
| Mean = 0.000868 | | | | | |

" k_1 " in the dark = 0.000662.

Therefore,

The value of " k_1 " in pure light in (i) = 0.000908

The value of " k_1 " in pure light in (ii) = .000378

The value of " k_1 " in pure light in (iii) = .000217

Result:—

| I. | II. If directly proportional to the intensity | III. If proportional to the square root of the intensity |
|----------------------------------------------------------------------------------------|--------------------------------------------------|-------------------------------------------------------------|
| $\frac{\text{Velocity (i)}}{\text{Velocity (ii)}} = \frac{0.000908}{.000378} = 2.40$ | 2.778 | 1.67 |
| $\frac{\text{Velocity (i)}}{\text{Velocity (iii)}} = \frac{0.000908}{.000217} = 4.19$ | 4.00 | 2.00 |
| $\frac{\text{Velocity (ii)}}{\text{Velocity (iii)}} = \frac{0.000378}{.000217} = 1.74$ | 1.44 | 1.17 |

From the above, it is clear that the reaction is directly proportional to the intensity of the incident light.

XIII. Ammonium oxalate and mercuric chloride (in presence of eosin as a sensitiser.)

Mercuric chloride — M/50; Ammonium oxalate — M/5; Eosin — M/20,500.

No light filter was used.

Temp. 21.5°C.

(i) Diameter of the aperture = 2.0 cm.

| Time in minutes | Gram-mol. of mercuric chloride per 3 c.c. | $1/2.3 \times k_1$ | Time in minutes | Gram-mol. of mercuric chloride per 3 c.c. | $1/2.3 \times k_1$ |
|-----------------|-------------------------------------------|--------------------|-----------------|-------------------------------------------|--------------------|
| 0 | 0.00002405 | — | 74 | 0.00001501 | 0.00278 |
| 36 | .00001904 | 0.00282 | | | Mean = 0.00279 |

(ii) Diameter of the aperture = 1.2 cm.

| Time in minutes | Gram-mol. of mercuric chloride per 3 c.c. | $1/2.3 \times k_1$ | Time in minutes | Gram-mol. of mercuric chloride per 3 c.c. | $1/2.3 \times k_1$ |
|-----------------|-------------------------------------------|--------------------|-----------------|-------------------------------------------|--------------------|
| 0 | 0.00002405 | — | 71 | 0.00001800 | 0.00177 |
| 34 | .00002099 | 0.00174 | 115 | .00001501 | .00178 |
| | | | | | Mean = 0.00176 |

(iii) Diameter of the aperture = 1.0 cm.

| Time in minutes | Gram-mol. of mercuric chloride per 3 c.c. | $1/2.3 \times k_1$ | Time in minutes | Gram-mol. of mercuric chloride per 3 c.c. | $1/2.3 \times k_1$ |
|-----------------|-------------------------------------------|--------------------|-----------------|-------------------------------------------|--------------------|
| 0 | 0.00002405 | — | 60 | 0.00001955 | 0.00150 |
| 28 | .00002173 | 0.00157 | 128 | .00001501 | .00161 |
| | | | | | Mean = 0.00156 |

Result:—

| I. | II. If directly proportional to incident intensity | III. If proportional to the square root of change of intensity |
|-------------------------------------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------------------|
| $\frac{\text{Velocity (i)}}{\text{Velocity (ii)}} = \frac{0.00279}{.00176} = 1.59$ | 2.78 | 1.67 |
| $\frac{\text{Velocity (i)}}{\text{Velocity (iii)}} = \frac{0.00279}{.00156} = 1.80$ | 4.00 | 2.00 |
| $\frac{\text{Velocity (I)}}{\text{Velocity (iii)}} = \frac{0.00176}{.00156} = 1.13$ | 1.44 | 1.17 |

From the above it is apparent that the rates of the reaction are proportional to the square roots of the ratios of the change of incident intensities.

XIV. Potassium permanganate and oxalic acid (in presence of manganous sulphate and sulphuric acid).

Potassium permanganate — N/444.4; Oxalic acid — N/32; Manganous sulphate — N/364.28; Sulphuric acid — N/2.7.

Filters 8 and 3 (λ 5000–4450 Å.).

Mean λ = 4725 Å.

Temp. 10°C.

(i) Diameter of the aperture = 2.0 cm.

| Time in minutes | Sodium thiosulphate per 3 c.c. of the reacting mixture | $1/2.3 \times k_1$ | Time in minutes | Sodium thiosulphate per 3 c.c. of the reacting mixture | $1/2.3 \times k_1$ |
|-----------------|--------------------------------------------------------|--------------------|-----------------|--------------------------------------------------------|--------------------|
| 0 | 3.625 c.c. | — | 3 | 1.0 c.c. | 0.186 |
| 1 | 2.35 | 0.188 | 3.9 | 0.75 | .183 |
| 2.17 | 1.45 | .183 | | Mean = 0.185 | |

(ii) Diameter of the aperture = 1.2 cm.

| Time in minutes | Sodium thiosulphate per 3 c.c. of the reacting mixture | $1/2.3 \times k_1$ | Time in minutes | Sodium thiosulphate per 3 c.c. of the reacting mixture | $1/2.3 \times k_1$ |
|-----------------|--------------------------------------------------------|--------------------|-----------------|--------------------------------------------------------|--------------------|
| 0 | 3.625 c.c. | — | 3.25 | 1.05 c.c. | 0.166 |
| 1 | 2.5 | 0.161 | 4.25 | 0.75 | .161 |
| 2.2 | 1.65 | .156 | | Mean = 0.161 | |

(iii) Diameter of the aperture = 1.0 cm.

| Time in minutes | Sodium thiosulphate per 3 c.c. of the reacting mixture | $1/2.3 \times k_1$ | Time in minutes | Sodium thiosulphate per 3 c.c. of the reacting mixture | $1/2.3 \times k_1$ |
|-----------------|--------------------------------------------------------|--------------------|-----------------|--------------------------------------------------------|--------------------|
| 0 | 3.625 c.c. | — | 3.83 | 1.0 c.c. | 0.146 |
| 1.17 | 2.5 | 0.147 | 4.83 | 0.75 | .142 |
| 2.42 | 1.65 | .142 | | Mean = 0.144 | |

" k_1 " in the dark at 10°C. = 0.0552.

Therefore,

The value of " k_1 " in pure light in (i) = 0.130

The value of " k_1 " in pure light in (ii) = .106

The value of " k_1 " in pure light in (iii) = .0888

Result:—

| | I. | II. If directly propor- tional to the intensity | III. If proportional to the square root of the intensity |
|-----------------------------------------------------------------------------------|----|----------------------------------------------------------|----------------------------------------------------------------------|
| $\frac{\text{Velocity (i)}}{\text{Velocity (ii)}} = \frac{0.130}{.106} = 1.23$ | | 2.78 | 1.67 |
| $\frac{\text{Velocity (i)}}{\text{Velocity (iii)}} = \frac{0.130}{.0888} = 1.46$ | | 4.00 | 2.00 |
| $\frac{\text{Velocity (ii)}}{\text{Velocity (iii)}} = \frac{0.106}{.0888} = 1.19$ | | 1.44 | 1.17 |

From the above table it is clear that though the velocity of this reaction increases appreciably with the increase in the intensity of the incident light yet there is no simple relation between the two.

XV. Quinine sulphate and chromic acid (in presence of sulphuric acid.)
 Quinine sulphate—M/75 in N/2 H₂SO₄; Chromic acid—M/80.88;
 Sulphuric acid—1.32 N.
 No light filter was used.
 Temp: 29°C.

(i) Diameter of the aperture = 1.6 cm.

| Time in minutes | Sodium thiosulphate per 3 c.c. of the reacting mixture | $1/2.3 \times k_1$ | Time in minutes | Sodium thiosulphate per 3 c.c. of the reacting mixture | $1/2.3 \times k_1$ |
|-----------------|--------------------------------------------------------|--------------------|-----------------|--------------------------------------------------------|--------------------|
| 0 | 6.15 c.c. | — | 35 | 4.2 c.c. | 0.00473 |
| 15 | 5.25 | 0.00458 | 58 | 3.2 | .00489 |
| | | | | | Mean = 0.00473 |

(ii) Diameter of the aperture = 1.2 cm.

| | | | | | |
|----|-----------|---------|----|----------|----------------|
| 0 | 6.15 c.c. | — | 48 | 5.2 c.c. | 0.00152 |
| 20 | 5.75 | 0.00146 | 70 | 4.8 | .00154 |
| | | | | | Mean = 0.00151 |

(iii) Diameter of the aperture = 1.0 cm.

| | | | | | |
|----|-----------|----------|----|-----------|-----------------|
| 0 | 5.15 c.c. | — | 42 | 5.65 c.c. | 0.000879 |
| 21 | 5.8 | 0.000857 | 85 | 5.2 | .000858 |
| | | | | | Mean = 0.000865 |

"k₁" in the dark at 29°C. = 0.000265.

Therefore,

The value of "k₁" in pure light in (i) = 0.00447

The value of "k₁" in pure light in (ii) = .00125

The value of "k₁" in pure light in (iii) = .000600

Result:—

| | I. | II. If proportional to the square of the incident intensity | III. If directly proportional to the intensity of the light |
|--------------------------------------------|--------|----------------------------------------------------------------------|-------------------------------------------------------------------------|
| Velocity (i) = $\frac{0.00447}{.00125}$ | = 3.58 | 3.33 | 1.77 |
| Velocity (ii) = $\frac{0.00447}{.000600}$ | = 7.45 | 6.55 | 2.56 |
| Velocity (iii) = $\frac{0.00125}{.000600}$ | = 2.83 | 2.47 | 1.44 |

It is apparent that the velocity of this reaction is proportional to the square of the intensity of the incident light within the limits of experimental error.

Discussion

From the foregoing results it will be seen that the reactions investigated in this paper can be divided into the following three classes with regard to the influence of the intensity of the incident light on the velocity of the reactions:—

| Velocity of the reactions proportional to the square of the intensity of the incident light | Velocity of the reactions proportional to the square root of the intensity of the incident light | Velocity of the reactions directly proportional to the intensity of the incident light |
|---------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|
| (i) Sodium formate and iodine | (i) Potassium oxalate and iodine | (i) Chromic acid and oxalic acid |
| (ii) Rochelle salt and bromine | (ii) Ammonium oxalate and iodine | (ii) Sodium citrate and iodine |
| (iii) Quinine sulphate and chromic acid | (iii) Sodium malate and iodine | (iii) Oxidation of iodoform in benzene medium |
| | (iv) Ammonium oxalate and mercuric chloride in presence of eosin | (iv) Sodium formate and mercuric chloride |
| | (v) Sodium nitrite and iodine | (v) Bleaching of dicyanin |

The reaction between potassium permanganate and oxalic acid is slightly influenced by light—the velocity changing at a ratio which is even less than the square root of the intensity of the incident light. There is also some difficulty in assigning a definite position to the reaction between ferrous sulphate and iodine in the above table.

It is very difficult to find out a theoretical significance for all these groups of reactions. If the velocities of the reactions in the dark are not deducted from the respective total values obtained in the light, the majority of the reactions involving iodine as one of the reactants fall into the second group, that is, the reaction velocities are proportional to the square root of the incident light.

Now, in the cases of reactions where iodine is one of the reacting substances, we have observed that the reactions are semimolecular with respect to iodine. It is very likely, therefore, that in all the reactions involving iodine as the photo-active constituent, the chemical changes take place between atoms of iodine. If we assume that in such reactions the atomic iodine is the photo-active substance then,

$$k_1 X [I_2] = k_2 [I]^2$$

$$\therefore [I] = \frac{k_1^{\frac{1}{2}}}{k_2^{\frac{1}{2}}} X^{\frac{1}{2}} [I_2]^{\frac{1}{2}}$$

where X is the intensity of the incident light and k_1 and k_2 are constants.

This explains that the rate of disappearance of iodine follows as the square-root of the intensity of the incident illumination.

It may be noted from the above table that the reactions placed in the second group—that is, the reactions whose velocity changes as the square root of the intensity are very prominently photochemical in nature. Such markedly photochemical changes when once started by light are not so much affected by increasing the intensity of illumination (as is evident by their velocities changing proportionally only as the square root of the intensity) as those reactions which are not so photosensitive.

The reactions between sodium formate and iodine and sodium citrate and iodine though semimolecular with respect to iodine do not fall in the second category. The reason for this may be attributed to the fact that neither of these reactions is so much accelerated by light as any of the changes placed in the second group. It is difficult to assign, however, any definite reason for the fact that while both the changes are not very remarkably photochemical in nature, the former reaction is so very sensitive to the influence of intensity as to change proportionally with its second power, whereas the latter, the reaction between sodium citrate and iodine, changes proportionally only as the first power of the intensity.

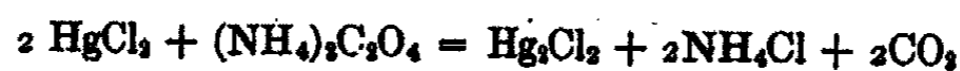
From our present state of knowledge it is also difficult to explain why, of all the other reactions investigated in this paper, the reaction between quinine sulphate and chromic acid though very markedly photosensitive is so profoundly affected by the variations in the intensity of the light as to change as the square of the intensity. It may be noted, however, that though the reaction is unimolecular with respect to the chromic acid, the reaction is quite complex and that the quinine sulphate solution also exhibits a marked absorption of light in the visible region.

Similar difficulty is felt in explaining the peculiar behavior of the reaction between potassium permanganate and oxalic acid in that the velocity of this change is very little affected by changing the intensity of the incident light.

In those cases where the velocities are directly proportional to the intensity of the incident light it may be pointed out that when the molecules become activated by the absorption of radiation they decompose or react without any further alteration and the velocities of the reactions change proportionally to the intensity of the incident radiation.

From the present series of experiments we have come to the conclusion that the reaction between mercuric chloride and ammonium oxalate is proportional to the square root of the intensity of the incident radiation. An explanation for such behavior can be offered as follows:—

In a previous paper¹ it has been proved that the reaction between mercuric chloride and potassium oxalate is bi-molecular in the dark, though the chemical change may be represented by the following equation:



In view of the above equation the reaction ought to be tri-molecular, whereas, it is found to be bi-molecular according to the kinetic measurements. It is apparent, that in the change taking place thermally the mercuric chloride molecules react in the polymerised form (Hg_2Cl_2) without dissociation, whereas, in the reaction taking place photochemically the Hg_2Cl_2 molecules break up into a pair of HgCl_2 molecules just as molecular iodine atomises into iodine atoms; and hence, this reaction is proportional to the square root of the incident radiation.

The bleaching of dicyanin and the oxidation of iodoform in benzene are directly proportional to the change in the intensity of the incident radiation.

Hence, it appears that when the molecules of iodoform and dicyanin become activated by the absorption of radiation, they decompose and the velocities of the reactions change proportionally to the intensity of the incident radiation. On the other hand, in the reaction between mercuric chloride and sodium formate, the velocity is directly proportional to the intensity of the incident radiation. It should be noted, however, that the reaction between ammonium oxalate and mercuric chloride is far more photosensitive than the reaction between mercuric chloride and sodium formate. Moreover, the velocity of the dark reaction between mercuric chloride and ammonium oxalate is practically negligible in comparison with the light reaction. Similarly the dark reaction velocity in the case of sodium malate and iodine is negligibly small in comparison with the reaction in the light. But the reaction between sodium formate and iodine proceeds in the dark at a rate which is appreciable in comparison with the light reaction.

It appears therefore, that the reactions which are really photochemical in nature are likely to be proportional to the square root of the intensity of the incident radiation. It seems reasonable to expect that in such reactions the

¹ Dhar: J. Chem. Soc., 111, 707, (1917).

velocities of the chemical change should not be altered a great deal when the reactions have started once by the absorption of the minimum quantity of energy. Hence, these reactions should be proportional to powers less than unity of the incident light.

As regards the reaction between potassium oxalate and iodine it may be remarked that the effect of the intensity of light on this reaction was not studied by Dhar as is generally assumed by some authors. It is only recently that we took up this investigation and the results are quite in line with the conclusions arrived at by Berthoud and Bellenot¹ and recently by Briers, Chapman and Walters². Proportionality between the intensity of light and the velocity has been found in the cases of the following reactions:—

Hydrolysis of chloroplatinic acid,³ the decomposition of hydrogen peroxide,⁴ the decompositions of potassium cobalti-oxalate⁵ and potassium mangani-oxalate⁶ and for the initial stages of the photolysis of the uranyl formate solutions.⁷

In all these cases it is difficult to imagine the reactant molecules to be breaking up into simpler constituents as the result of the absorption of light. Hence it is expected that in all these changes the velocities of the reactions would be directly proportional to the intensity of the incident radiation.

In the reaction between chlorine and hydrogen there is considerable difference of opinion among different workers with regard to the influence of the incident radiation on the velocity of the chemical change. M.C.C. Chapman,⁸ Marshall⁹ and Kornfeld and Müller¹⁰ have upheld that the reaction is directly proportional to the incident radiation. On the other hand Berthoud¹¹ suggests that the reaction is proportional to the square root of the intensity. Baly and Barker¹² however, support that the reaction is proportional to $(I)^{3/2}$. It is very difficult to differentiate between these divergent results. If the reaction velocity be dependent on the square root of the intensity it can be assumed that the chlorine molecules are first dissociated into atoms.

Now the heat of dissociation of chlorine molecules is 55,000 calories corresponding to the wave length 0.52μ . It is well known that the mixture of hydrogen and chlorine combines in sun light and in that light the mean wave length in the visible region is about 5000 \AA . It seems quite possible that even in the combination of chlorine and hydrogen, atoms of chlorine take part and

¹ Helv. Chim. Acta, 7, 307 (1924).

² J. Chem. Soc., 129, 562 (1926).

³ Ann. phys. (9) 2, 5, 226 (1914).

⁴ Tian: Ann. phys., (9) 5, 248 (1916).

⁵ J. Vránek: Z. Elektrochemie, 23, 336 (1917).

⁶ Ghosh and Kappana: J. Ind. Chem. Soc., 3, 127 (1926).

⁷ E. C. Hatt: Z. physik. Chem., 92, 513 (1918).

⁸ J. Chem. Soc., 125, 1521 (1924).

⁹ J. Phys. Chem., 29, 842 (1925).

¹⁰ Unpublished data.

¹¹ Helv. Chim. Acta, 7, 324 (1924).

¹² J. Chem. Soc., 119, 653 (1926).

the reaction velocity is proportional to the square root of the intensity of the light.

In this connection it will be interesting to observe that Bodenstein and Lütke Meyer¹ have shown that the rate of reaction between hydrogen and bromine is proportional to the square root of the light absorbed.

It is difficult to assign any reason for the facts that the reactions between quinine sulphate and chromic acid, rochelle salt and bromine, and sodium formate and iodine proceed at rates which are proportional to the square of the intensity of the incident light. As far as we know no such case has been recorded before. The only reaction where the velocity is proportional to the intensity of radiation to a power greater than unity is the photo-combination of hydrogen and chlorine as investigated by Baly and Barker. Unfortunately the theoretical significance of such behaviour is still uncertain.

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¹Z. physik. Chem., 114, 208 (1924).

SOLUBILITY RELATIONS OF ISOMERIC ORGANIC COMPOUNDS

VIII. Solubility of the Aminobenzoic Acids in Various Liquids

BY CHARLES L. LAZZELL* AND JOHN JOHNSTON

In a previous paper¹ there were presented series of measurements of the solubility of the three nitroanilines in water, alcohol, benzene, chloroform, carbon tetrachloride, ether, ethyl acetate and acetone; the corresponding solubility curves for the three isomers are in general very similar, yet differ appreciably in some cases, these differences being evidently somehow correlated with the melting temperature (presumably also with the heat of melting) of the crystalline isomer. These results indicated the desirability of investigating similarly a related series of isomers to learn more as to the degree of similarity which may be expected in such parallel cases. Consequently we have measured the solubility, in the same solvents, of the three aminobenzoic acids, which differ formally from the nitroanilines only in the substitution of a carboxyl group for a nitro group; in chemical behavior they differ specifically in the pronounced amphoteric character of the aminobenzoic acids in aqueous solution, and in the readiness with which they decompose at elevated temperatures.

There are few data available on the solubility of the aminobenzoic acids. Flaschner and Rankin² determined the solubility of each in water at temperatures ranging in the case of the *ortho* from 84°, of *meta* from 66°, of *para* from 47°, up to the respective melting point; de Coninck³ worked with the *meta* in water from 0°–70°, and there are scattered data in various solvents at temperatures 10°–25°. The solvents used in the work here presented are methyl, ethyl, and butyl alcohol, ethyl acetate, benzene and chloroform; the temperature range is from 25° to the melting temperature of the respective acid except in the case of butyl alcohol in which fewer measurements were made.

The materials used, selected from the purest stock obtainable, were purified as follows:

Ortho-aminobenzoic Acid. The C.P. acid was crystallized several times from water at about 80°, boiling water being avoided because at that temperature some decomposition of the acid occurs.⁴ Norite was used as a decolorizer prior to the first crystallization from water. Finally the acid was crystallized from hot chloroform, which yielded a slightly yellow crystalline material. A white product can be obtained if the acid is sublimed, but

* From a part of the dissertation presented to the Graduate School of Yale University, in June, 1927, by Charles L. Lazzell in candidacy for the degree of Doctor of Philosophy.

¹ Collett and Johnston: *J. Phys. Chem.*, 30, 70 (1926).

² Flaschner and Rankin: *Monatshft*, 31, 23 (1910).

³ Oechsner de Coninck: *Compt. rend.*, 116, 758 (1893).

⁴ MacMaster and Shriner: *J. Am. Chem. Soc.*: 45, 571 (1923).

there is some decomposition, which necessitates a further crystallization from water. The melting point of the acid as purified was 146.1°; that given in the literature is 144°-145°. The melting points given in this paper were determined by the usual capillary tube method; all readings were corrected for emergent stems and the thermometers used were compared with thermometers certified by the Bureau of Standards.

Meta-aminobenzoic Acid. The C.P. acid was crystallized several times from hot water, then from 95% ethyl alcohol, and finally from boiling water, which in this case causes no decomposition. The *meta* acid can readily be

TABLE I

Final Experimental Values of the Solubility, in Terms of Molal Percentage, of *ortho*-Aminobenzoic Acid in:—

| a) Benzene | | b) Ethyl Alcohol | |
|------------|-------|------------------|-------|
| C | t | C | t |
| 100.00 | 146.1 | 100.00 | 146.1 |
| 80.64 | 135.2 | 73.92 | 125.5 |
| 71.26 | 129.9 | 38.19 | 93.9 |
| 64.69 | 126.3 | 33.03 | 86.5 |
| 61.74 | 125.1 | 26.94 | 77.3 |
| 50.88 | 119.6 | 22.19 | 68.2 |
| 51.03 | 119.3 | 7.75 | 25.0 |
| 34.96 | 110.3 | | |
| 29.26 | 108.3 | | |
| 22.22 | 101.6 | | |
| 16.35 | 93.3 | | |
| 13.13 | 89.5 | | |
| 8.71 | 75.7 | | |
| 0.81 | 25.0 | | |

| e) Chloroform | | d) Ethyl Acetate | |
|---------------|-------|------------------|-------|
| C | t | C | t |
| 100.00 | 146.1 | 100.00 | 146.1 |
| 43.14 | 110.8 | 65.03 | 120.8 |
| 29.07 | 100.4 | 52.82 | 108.0 |
| 18.83 | 88.9 | 29.73 | 76.8 |
| 11.24 | 76.5 | 14.71 | 25.0 |
| 1.57 | 25.0 | | |

| e) Methyl Alcohol | | f) Butyl Alcohol | |
|-------------------|-------|------------------|-------|
| C | t | C | t |
| 100.00 | 146.1 | 100.00 | 146.1 |
| 25.92 | 77.1 | 44.86 | 104.6 |
| 13.70 | 50.7 | 26.80 | 80.1 |
| 7.62 | 25.0 | | |

TABLE II
Final Experimental Values of the Solubility, in Terms
of Molal Percentage, of *meta*-Aminobenzoic Acid in:—

| a) Benzene | | b) Ethyl Alcohol | |
|-------------------|-------|------------------|-------|
| C | t | C | t |
| 100.00 | 177.9 | 100.00 | 177.9 |
| 67.04 | 161.7 | 78.06 | 163.6 |
| 34.92 | 156.7 | 47.92 | 140.5 |
| 19.54 | 153.5 | 24.11 | 115.5 |
| 12.60 | 150.4 | 11.89 | 98.6 |
| 7.54 | 143.7 | 1.52 | 25.0 |
| 5.53 | 138.5 | | |
| 4.23 | 134.4 | | |
| 0.008 | 25.0 | | |
| c) Chloroform | | d) Ethyl Acetate | |
| C | t | C | t |
| 100.00 | 177.9 | 100.00 | 177.9 |
| 32.13 | 152.7 | 47.19 | 145.1 |
| 5.63 | 132.9 | 11.76 | 110.5 |
| 3.65 | 124.8 | 1.30 | 25.0 |
| 0.05 | 25.0 | | |
| e) Methyl Alcohol | | f) Butyl Alcohol | |
| C | t | C | t |
| 100.00 | 177.9 | 100.00 | 177.9 |
| 20.07 | 109.6 | 29.35 | 138.7 |
| 9.73 | 86.2 | 20.72 | 127.2 |
| 1.70 | 25.0 | | |

sublimed in vacuo, yielding a very pure product. The product from either crystallization or sublimation was perfectly white, and had a melting point of 177.9°; that given in the literature is 174°.

Para-aminobenzoic Acid. The C.P. acid was crystallized several times from water at 80°, boiling water causing decomposition as in the case of the *ortho* acid, then from 95% ethyl alcohol, and finally from water at 80°. Upon slow cooling the crystals came out of water in long colorless needles, which color slightly upon exposure to light; they have a melting point of 187°, which is the same as given in the literature, 186°–187°.

The mode of purification of the several solvents was identical with that described in the earlier paper and so need not be repeated here except to note that the methyl alcohol boiled at 66.5°–67° at 765 mm., and the butyl alcohol at 116.5° at 760 mm. The method of experiment was also identical with that previously described; the only difference being that in the analytical method, used only at 25°, a weighed sample of the saturated solution was titrated with 0.1 molar sodium hydroxide previously standardized against the pure acid. The results are again satisfactorily concordant throughout the range. The solubility of each of the three aminobenzoic acids was de-

TABLE III
Final Experimental Values of the Solubility, in Terms
of Molal Percentage, of *para*-Aminobenzoic Acid in:—

| a) Benzene | | b) Ethyl Alcohol | |
|-------------------|-------|------------------|-------|
| C | t | C | t |
| 100.00 | 187.0 | 100.00 | 187.0 |
| 53.42 | 165.0 | 65.52 | 155.2 |
| 32.37 | 160.2 | 48.01 | 140.1 |
| 28.50 | 159.8 | 30.00 | 115.0 |
| 18.24 | 156.5 | 22.04 | 99.0 |
| 15.66 | 155.2 | 20.04 | 88.7 |
| 14.14 | 154.8 | 15.29 | 81.3 |
| 4.98 | 139.9 | 13.56 | 75.8 |
| 2.11 | 121.7 | 4.97 | 25.0 |
| 0.04 | 25.0 | | |
| c) Chloroform | | d) Ethyl Acetate | |
| C | t | C | t |
| 100.00 | 187.0 | 100.00 | 187.0 |
| 29.90 | 156.4 | 48.40 | 144.0 |
| 5.25 | 136.7 | 41.95 | 136.6 |
| 0.13 | 25.0 | 34.75 | 131.2 |
| | | 23.07 | 112.1 |
| | | 12.19 | 82.1 |
| e) Methyl Alcohol | | f) Butyl Alcohol | |
| C | t | C | t |
| 100.00 | 187.0 | 100.00 | 187.0 |
| 26.87 | 108.3 | 55.10 | 153.2 |
| 17.75 | 86.5 | 33.36 | 134.5 |
| 5.94 | 25.0 | | |

terminated over the range from 25° upwards in benzene, chloroform, ethyl alcohol; a less complete series with ethyl acetate, methyl alcohol, butyl alcohol; the last two constituting with ethyl alcohol a group of closely related solvents. The final experimental results are presented in Tables I-III, C being the molal percentage ($C = 100N$ where N is the mole fraction) and t the temperature centigrade.

These data were plotted on a large scale in terms of C versus t ; from these curves were read off, at 10° intervals, values of the solubility, and these are listed in Table IV, the sequence of solvents being in order of diminishing solubility of the respective acid in the lower part of the temperature range. The values for water are derived similarly from the data of Flaschner and Rankin: those in the column headed "Ideal" were calculated from the integrated form of the solubility equation on the basis that the molal heat of melting, and its dependence upon temperature, is expressed by the following equation, derived directly from calorimetric data¹:

¹ Andrews, Lynn and Johnston: *J. Am. Chem. Soc.*, 48, 1274 (1926). Details of the method of calculation may be found in *J. Phys. Chem.*, 29, 1041 (1925).

TABLE IV

Solubility of the Aminobenzoic Acids in Various Solvents, as Interpolated at a Series of Temperatures, expressed in Terms of Mol Percentage, C.

| Temp. | Ideal | EtOAc | a) <i>ortho</i> (m.p. 146.1°) | | | | | H ₂ O* |
|-------|-------|--------|----------------------------------|--------------------|------------|-------------------|-------------------------------|-------------------|
| | | | C ₂ H ₅ OH | CH ₃ OH | Butyl Alc. | CHCl ₃ | C ₆ H ₆ | |
| 25 | 11.3 | 14.71 | 7.75 | 7.62 | | 1.57 | 0.81 | |
| 30 | 12.6 | 15.2 | 9.0 | 8.6 | | 2.0 | 1.3 | |
| 40 | 15.5 | 16.8 | 11.6 | 10.8 | | 3.0 | 2.3 | |
| 50 | 19.0 | 19.2 | 14.6 | 13.5 | | 4.4 | 3.6 | |
| 60 | 23.2 | 22.2 | 18.5 | 17.2 | | 6.4 | 5.3 | |
| 70 | 28.2 | 26.2 | 23.0 | 22.1 | | 9.0 | 7.2 | |
| 80 | 34.1 | 31.6 | 28.4 | 27.8 | 26.6 | 13.0 | 9.9 | 0.6 |
| 90 | 40.9 | 39.0 | 35.2 | (35.0) | 32.6 | 19.5 | 13.5 | .9 |
| 100 | 48.7 | 45.8 | 43.8 | (43.5) | 40.0 | 28.5 | 20.0 | 2.4 |
| 110 | 57.7 | 54.4 | 54.4 | (53.9) | 52.0 | 41.8 | 34.3 | 31.2 |
| 120 | 67.8 | 64.6 | 67.0 | (66.7) | (65.3) | 57.9 | 52.5 | 55.2 |
| 130 | 79.2 | (77.7) | 79.6 | (79.4) | (78.6) | (72.0) | 70.6 | 74.2 |
| 140 | 91.7 | (91.5) | 92.3 | (92.2) | (91.9) | (90.1) | 88.8 | 91.8 |

*From Flaschner and Rankin, m.p. 144.6°C. Values extrapolated much beyond the experimental range where the slope of the curve seems uncertain are enclosed in parentheses.

| Temp. | Ideal | b) <i>meta</i> (m.p. 177.9°) | | | | | H ₂ O* | |
|-------|-------|------------------------------|----------------------------------|--------|-----------|-------------------|-------------------|-------------------------------|
| | | CH ₃ OH | C ₂ H ₅ OH | EtOAc | Butyl Alc | CHCl ₃ | | C ₆ H ₆ |
| 25 | 6.3 | 1.70 | 1.52 | 1.30 | | 0.05 | 0.008 | 0.1 |
| 30 | 7.0 | 2.2 | 1.8 | 1.4 | | .3 | .2 | .2 |
| 40 | 8.8 | 3.4 | 2.5 | 1.6 | | .7 | .4 | .3 |
| 50 | 10.9 | 4.6 | 3.2 | 1.8 | | 1.1 | .7 | .4 |
| 60 | 13.5 | 5.7 | 4.0 | 2.0 | | 1.5 | 1.0 | .5 |
| 70 | 16.5 | 7.0 | 4.6 | 2.5 | | 1.9 | 1.3 | .6 |
| 80 | 20.2 | 8.6 | 6.0 | 3.3 | | 2.2 | 1.6 | .7 |
| 90 | 24.5 | 10.8 | 8.4 | 4.7 | | 2.5 | 1.8 | .9 |
| 100 | 29.5 | 15.0 | 12.7 | 6.8 | | 2.8 | 2.2 | 1.4 |
| 110 | 35.4 | 20.3 | 19.7 | 11.4 | | 3.1 | 2.4 | 3.5 |
| 120 | 42.1 | 27.9 | 27.9 | 19.2 | | 3.4 | 2.7 | 12.6 |
| 130 | 49.7 | 37.5 | 37.3 | 28.4 | 22.4 | 4.8 | 3.6 | 26.3 |
| 140 | 58.3 | (48.7) | 47.4 | 39.8 | 30.6 | 9.5 | 5.9 | 39.9 |
| 150 | 67.8 | (61.0) | 59.0 | 54.6 | | 23.3 | 12.1 | 54.0 |
| 160 | 78.4 | (73.9) | 72.8 | (70.9) | | (68.9) | (59.7) | 70.0 |
| 170 | 90.1 | (88.0) | 88.0 | (87.1) | | (88.0) | (88.0) | 87.0 |

*From Flaschner and Rankin, m.p. 174.4; values below 67° from de Coninck.

TABLE IV (continued)

| Temp. | Ideal | o) <i>para</i> (m.p. 187.0°) | | | | | | |
|-------|-------|------------------------------|----------------------------------|--------|------------|-------------------|-------------------------------|------------------|
| | | CH ₃ OH | C ₂ H ₅ OH | EtOAc | Butyl Alc. | CHCl ₃ | C ₆ H ₆ | H ₂ O |
| 25 | 7.1 | 5.94 | 4.97 | 5.1 | | 0.13 | 0.04 | 0.7 |
| 30 | 7.9 | (6.6) | 5.4 | 5.4 | | (.2) | .2 | .2 |
| 40 | 9.6 | (8.2) | 6.5 | 6.0 | | (.4) | .3 | |
| 50 | 11.7 | (9.6) | 7.8 | 7.0 | | (.7) | .4 | |
| 60 | 14.1 | (11.4) | 9.5 | 8.1 | | (1.0) | .6 | |
| 70 | 17.0 | 13.4 | 11.8 | 9.7 | | (1.2) | .7 | |
| 80 | 20.4 | 15.8 | 14.8 | 11.7 | | (1.5) | .8 | 0.7 |
| 90 | 24.3 | 19.0 | 18.4 | 14.3 | | (1.8) | 1.0 | 1.1 |
| 100 | 28.8 | 22.9 | 22.4 | 17.7 | | (2.1) | 1.2 | 2.4 |
| 110 | 33.9 | 27.7 | 27.3 | 22.0 | | (2.4) | 1.4 | 6.2 |
| 120 | 39.8 | 33.8 | 33.1 | 27.8 | | (2.6) | 2.0 | 17.0 |
| 130 | 46.1 | (41.1) | 40.4 | 35.4 | 28.7 | (3.0) | 3.0 | 31.7 |
| 140 | 53.8 | (49.8) | 49.7 | 44.4 | 39.3 | 7.2 | 5.0 | 45.2 |
| 150 | 62.0 | (59.6) | 59.9 | 54.8 | 51.1 | 18.3 | 10.0 | 58.6 |
| 160 | 71.1 | (70.1) | 70.8 | (66.3) | 63.7 | 38.0 | 30.3 | 72.0 |
| 170 | 81.0 | (80.9) | (81.6) | (78.8) | (76.7) | (73.8) | 68.4 | 84.3 |
| 180 | 91.9 | 92.0 | (92.4) | (91.3) | (90.3) | (92.3) | (90.0) | 94.6 |

* From Flaschner and Rankin, m.p. 186.0.

$$\textit{ortho} : \Delta H = 3192 + 25.13t - 0.0934t^2$$

$$\textit{meta} : \Delta H = 3389 + 25.29t - 0.084t^2$$

$$\textit{para} : \Delta H = 3082 + 21.56t - 0.0603t^2$$

The corresponding values of the coefficients in the ideal equation

$$\log N_A = K_1 \left(\frac{T_A - T}{T} \right) + K_2 \log \frac{T_A}{T} + K_3 (T_A - T)$$

are:

| | T _A | K ₁ | K ₂ | K ₃ |
|--------------|----------------|----------------|----------------|----------------|
| <i>ortho</i> | 419.2 | 5.546 | -38.32 | 0.02042 |
| <i>meta</i> | 451.0 | 4.741 | -35.82 | 0.01836 |
| <i>para</i> | 460.1 | 3.470 | -27.43 | 0.01318 |

Discussion of Results

There is again a general similarity in shape between the solubility curve of each of the three aminobenzoic acids in any one solvent, as is apparent from Fig. 1. The curves for the *meta* and *para* isomers in water, benzene and chloroform exhibit reverse curvature, implying an approach to the region of two liquid layers; in the case of the *ortho*, this characteristic is marked only with water, though with benzene there is an indication of similar behavior. The general similarity of the curves led us in this case again¹ to seek some function of the solubility which would yield super-

¹ Cf. Collett and Johnston: *loc. cit.*, p. 80.

possible curves; but none of these attempts succeeded. Nor did we find it possible to superpose the corresponding curves for the aminobenzoic acids and the nitroanilines. There are therefore real differences between the curves, associated with specific differences in the chemical nature of both solute and solvent.

The order of the several liquids with respect to their solvent power is, for the lower, and larger, part of the temperature range, that of the corresponding set of column headings in Table IV. This order is the same except for

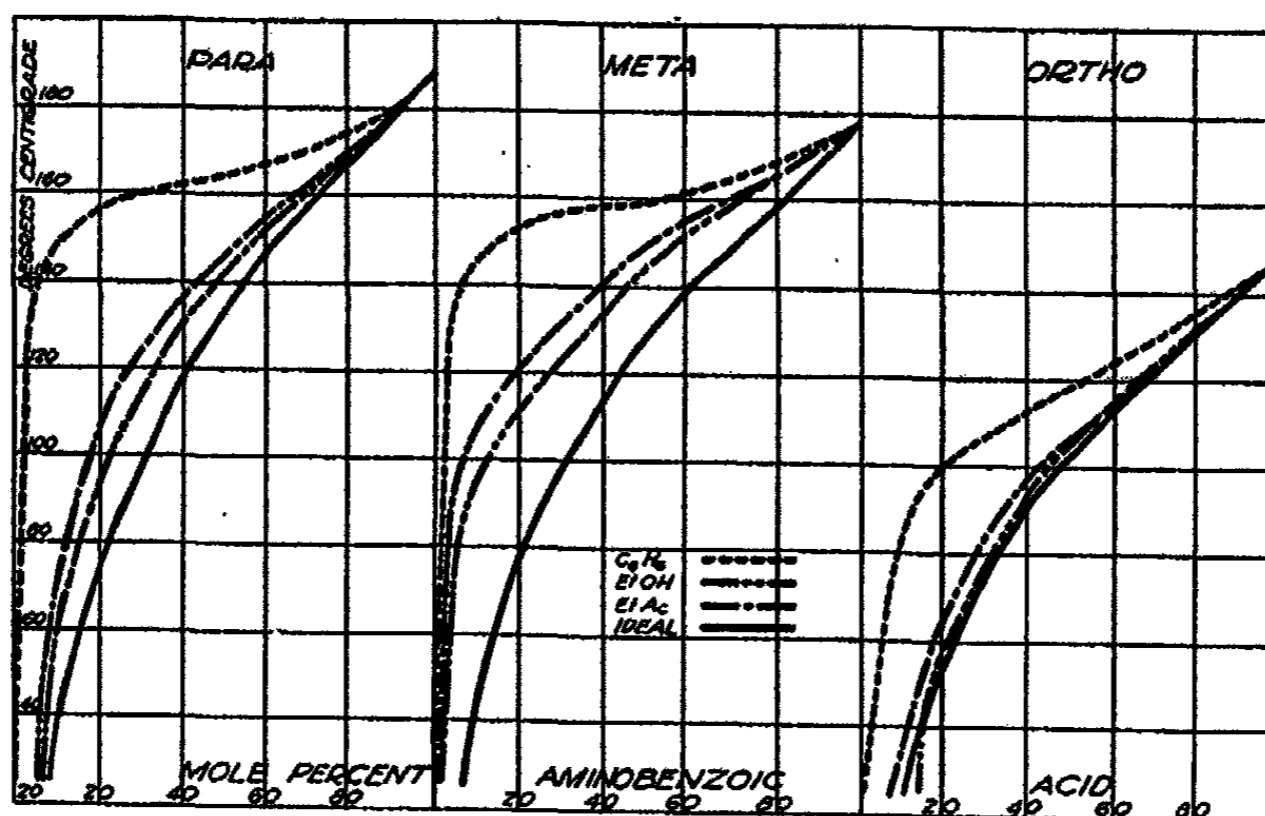


FIG. 1

the *ortho* in ethyl acetate, ethyl and methyl alcohols at the lower temperatures. The solubility of the *ortho* is greatest in ethyl acetate up to about 110° , at which point (about 35° below the melting point of the solid acid) it is exceeded by that in the methyl and ethyl alcohols, and thereafter the order for all three isomers is the same. The solubility of each isomer is nearly the same in ethyl as in methyl alcohol; for *ortho* ethyl is slightly better, for *meta* methyl is somewhat better, and for *para* the pair of curves cross at about 140° . The order of solubility of *para*-nitroaniline in the five solvents common to both investigations is the same as that of *ortho*-aminobenzoic acid; but the *ortho*- and *meta*-nitroanilines each show a different order as between chloroform, benzene and ethyl alcohol. It is again apparent therefore that one is not justified in assigning an order of solvent power to a series of liquids, based on gradations in their physical properties, even when one is dealing with solutes as closely related as those under discussion.

If now we consider the course of the curves downwards from the melting temperature of the solute, we find that initially all are close to one another and to the ideal, but that they soon diverge and separate into two groups.

The first group, nearer the ideal, comprises the more polar liquids, ethyl acetate, the three alcohols (and water at the higher temperatures); the second, further from the ideal, comprises the less polar liquids, chloroform and benzene, the last being (with the exception of water) the poorest solvent in all cases. With the, presumably less polar, nitroanilines as solutes, this grouping of solvents is less well marked, the alcohol curve occupying an intermediate position.

Instead of comparing solubilities at a fixed temperature, it is perhaps more logical to make the comparison at a fixed distance below the melting tempera-

TABLE V
Solubility of the Hydroxybenzoic Acids in Several Solvents at a Series of Temperatures, interpolated from the data of Sidgwick and Ewbank¹; in terms of Mol Percentage.

| Temperature | 99% C ₂ H ₅ OH | A. <i>ortho</i> (m.p. 159.0°) | | | | Water |
|-------------|--------------------------------------|-------------------------------|---------|---------|--------|-------|
| | | Butyl Alc. | Benzene | Heptane | | |
| 50 | 21.5 | 21.1 | 1.0* | — | 0.07** | |
| 70 | 28.1 | 27.8 | 2.4 | — | 0.2 | |
| 90 | 36.6 | 35.9 | 7.3 | 1.3 | .4 | |
| 110 | 48.1 | 47.6 | 23.2 | 3.5 | 20.5 | |
| 130 | 65.2 | (65.4) | 47.6 | 11.1 | 50.3 | |
| 150 | 88.7 | — | 88.2 | (77.5) | (84.5) | |
| | | B. <i>meta</i> (m.p. 201.3°) | | | | |
| 70 | 18.8 | | | | 0.9† | |
| 90 | 22.0 | 20.8 | | | 3.4 | |
| 110 | 26.5 | 25.5 | | | 10.9 | |
| 130 | 33.6 | 32.4 | 0.9 | Triple | 22.2 | |
| 150 | 44.6 | 42.8 | 2.2 | point | 36.3 | |
| 170 | 60.8 | 62.8 | 11.4 | 197° | | |
| 190 | 85.3 | (86.5) | 66.8 | | | |
| | | C. <i>para</i> (m.p. 213.0°) | | | | |
| 70 | 18.2 | 16.4 | | | 0.9† | |
| 90 | 22.5 | 20.2 | | | 3.2 | |
| 110 | 27.0 | 24.6 | | Triple | 10.5 | |
| 130 | 32.6 | 29.5 | 0.5 | point | 20.4 | |
| 150 | 39.8 | 36.0 | 1.3 | 208.5° | 31.6 | |
| 170 | 49.0 | 49.0 | 3.6 | | 45.6 | |
| 190 | 68.0 | 71.4 | 14.2 | | (66.9) | |

* Includes data at temperatures 12–64° by Walker and Wood: J. Chem. Soc., 73, 618 (1898).

** Includes data by Walker and Wood (loc. cit.), by Flaschner and Rankin (loc. cit.), and by Alexejew, Wied. Ann. 28, 305 (1886). On undercooling two liquid layers are realized; critical solution temperature 89.5° (S. and E.).

† Includes data by Walker and Wood, and by Flaschner and Rankin.

¹ Figures in brackets are extrapolated.

ture of the solute. If this is done, the order of decreasing solubility in ethyl alcohol is *para*, *ortho*, *meta*, whereas in benzene it is *ortho*, *para*, *meta* over a range of 60° below the melting temperature but *ortho*, *meta*, *para* at lower temperatures. Thus it appears that the relative solubility of a group of isomers cannot safely be inferred from the order of their melting temperatures, but depends also upon factors associated with the difference in their chemical properties. As an illustration of this statement the *ortho* and *para*, with chemical properties similar in many respects, show similar curves in ethyl alcohol, whereas the *meta*, with rather different properties, shows a somewhat different type of curve; this is true for the nitroanilines as well as for the aminobenzoic acids.

TABLE VI

Solubility of the Nitrobenzoic Acids, in terms of Mol Percentage, from the data of Sidgwick and Ewbank.

| Temp. | <i>ortho</i> (m.p. 146.8°) | | | <i>meta</i> m.p. 141.4° | | | <i>para</i> (m.p. 242.4°) | | |
|-------|-------------------------------|--------------------------------|-------------------|-------------------------------|--------------------------------|-------------------|-------------------------------|--------------------------------|-------------------|
| | C ₆ H ₆ | C ₇ H ₁₆ | H ₂ O* | C ₆ H ₆ | C ₇ H ₁₆ | H ₂ O* | C ₆ H ₆ | C ₇ H ₁₆ | H ₂ O* |
| 50 | | | 0.2 | 2.6 | | T. P | | | |
| 70 | 1.4 | | 0.9 | 6.0 | | 76.8° | | | |
| 90 | 4.8 | | 28.8 | 17.4 | | 33.2 | | | |
| 110 | 24.6 | Triple | 49.8 | 45.5 | Triple | 55.0 | | | |
| 130 | 69.7 | point | 77.0 | 80.1 | point | 83.0 | | | 0.1 |
| 150 | | 139.6° | | | 135° | | | | 0.6 |
| 170 | | | | | | | 5.2 | Triple | 13.5 |
| 190 | | | | | | | 14.6 | point | 35.6 |
| 210 | | | | | | | 49.0 | 234° | (60.1) |

* Includes data by Flaschner and Rankin.

TABLE VII

Solubility of the Chlorobenzoic Acids, in terms of Mol Percentage, from the data of Sidgwick and Ewbank (for benzene and heptane) and of Flaschner and Rankin (for water).

| Temp. | <i>ortho</i> (m.p. 140.3°) | | | <i>meta</i> (m.p. 154.5°) | | | <i>para</i> (m.p. 241.5°) | | |
|-------|-------------------------------|--------------------------------|------------------|-------------------------------|--------------------------------|------------------|-------------------------------|--------------------------------|------------------|
| | C ₆ H ₆ | C ₇ H ₁₆ | H ₂ O | C ₆ H ₆ | C ₇ H ₁₆ | H ₂ O | C ₆ H ₆ | C ₇ H ₁₆ | H ₂ O |
| 50 | 3.5 | | | 2.3 | | | | | |
| 70 | 9.5 | | | 6.2 | 1.1 | | | | |
| 90 | 23.6 | 2.4 | * | 14.6 | 3.0 | | 0.9 | | |
| 110 | 47.6 | 6.8 | 38.8 | 34.8 | 7.9 | * | 1.9 | | |
| 130 | 84.1 | 60.0 | 80.2 | 61.9 | 26.7 | 44.6 | 4.0 | 1.0 | |
| 150 | | | | 93.2 | (90.4) | 87.2 | 8.4 | 1.7 | |
| 170 | | | | | | | 26.5 | 4.0 | 0.8 |
| 190 | | | | | | | 31.6 | 10.4 | 16.1 |
| 210 | | | | | | | 53.8 | 25.7 | (49.6) |

* Two liquid layers.

Comparison may also be made with the data of Sidgwick and Ewbank¹ on the solubility of each of the three hydroxybenzoic acids in water, 99% ethyl alcohol, butyl alcohol, benzene and heptane; of the nitrobenzoic acids in water, benzene and heptane; and of the chlorobenzoic acids in benzene and heptane. Their results, originally in terms of weight percentages, have been computed in terms of mols, and plotted along with such other data as are available; values interpolated at even temperatures are presented in Tables V-VII, the solvents being arranged in order of diminishing solvent power.

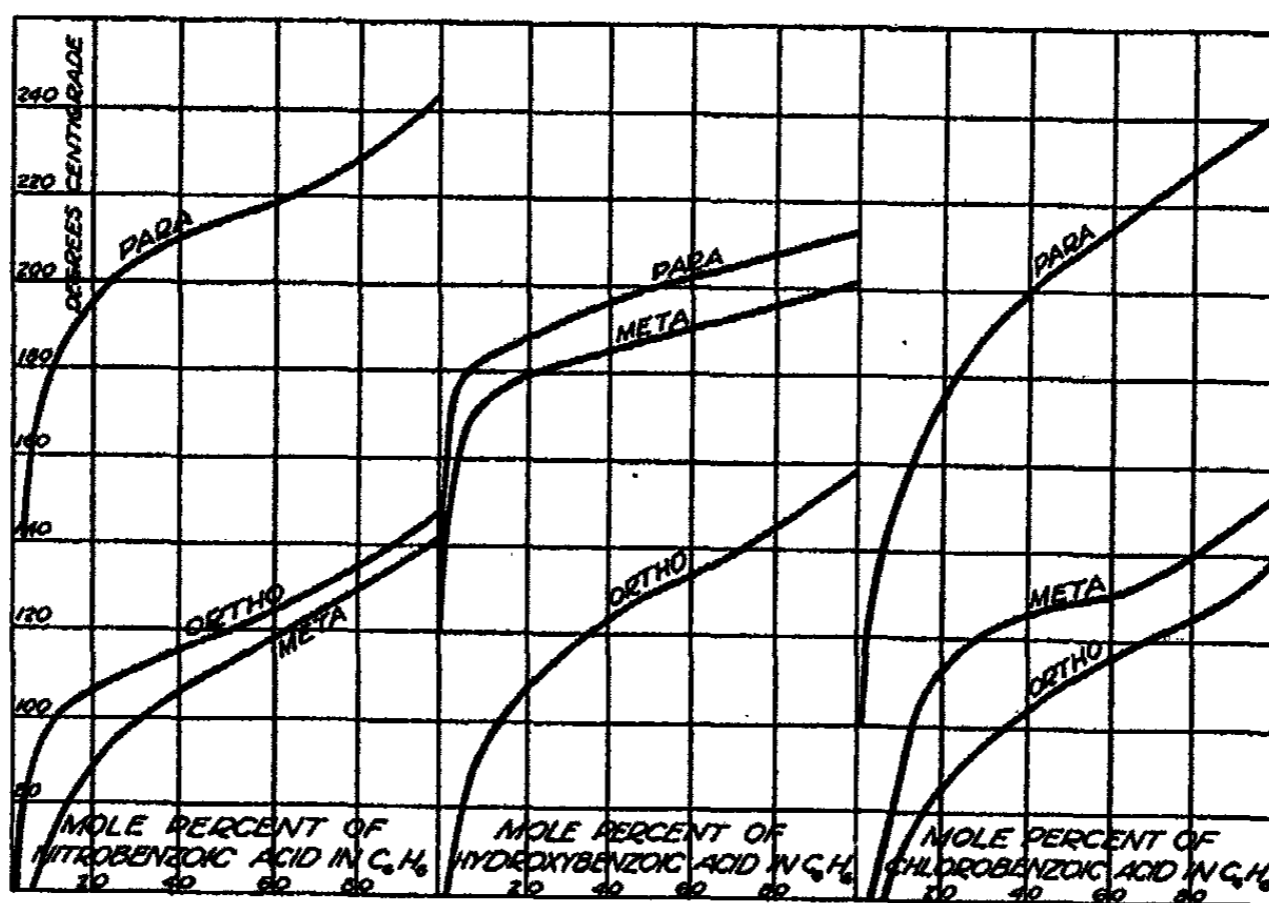


FIG. 2

The curves for these sets of isomers in benzene as solvent are shown in Fig. 2. In these cases the solubility curves again exhibit the same kind of disparities although superficially there is a general similarity. The hydroxybenzoic acids are each about equally soluble in ethyl alcohol (99%) and in butyl alcohol, but much less soluble in benzene. The solubility in heptane is much less than in benzene, for all of these groups of acids; in water the order of solubility is irregular, as might be expected from the appearance of two liquid layers in some of the systems. Moreover there is no obvious relation between solubility and the melting temperature of the solute, although it does happen in some instances that solutes which melt about the same temperature have nearly identical solubility curves in some solvent over a considerable range of temperature.

No one solvent seems to offer any special advantage in the separation of the isomers by recrystallization; for the ratio of the temperature co-

¹Sidgwick and Ewbank: J. Chem. Soc., 119, 979 (1921).

efficients of solubility is about the same for each of the isomers, in any one solvent, within the practical temperature limits imposed by the boiling point of the solvent.

Summary

The solubility curves for each of the three aminobenzoic acids was determined, from 25° to the respective melting temperature, in benzene, chloroform, ethyl alcohol, and ethyl acetate. A few determinations were made in butyl alcohol and in methyl alcohol in order to ascertain the position of these curves relative to that for ethyl alcohol. The determinations at 25° were made by the analytical method, all others by the synthetic method.

The results are discussed briefly, and compared with similar solubility data, from other sources, on other mono-substituted benzoic acids and on the nitroanilines. Many of the corresponding curves are very similar in general shape, but there are many departures which indicate that the solubility, even of closely related compounds, is influenced by the specific chemical nature of both solvent and solute.

STUDIES IN THE EXPERIMENTAL TECHNIQUE OF PHOTOCHEMISTRY

VI. The Energy Distribution of the Uviol Lamp

BY E. BEESLEY AND H. N. RIDYARD

Introduction

The Uviol lamp, formerly used as the light source in many researches in photochemistry, was the subject of energy distribution determinations by Allmand¹, who also described previous attempts in this direction. Owing to the low intensity of the radiation from this lamp, and troubles due to the unsteadiness of the Paschen galvanometer used, the deflections he was able to obtain were very small, and the possibility of error correspondingly large. Although this lamp is not likely to be much used in future, it seemed to be of interest to redetermine its energy distribution, as a much more sensitive arrangement of apparatus was available in this laboratory. It was hoped that the results obtained might usefully be applied to some of the published work in which this lamp was used. An examination of these papers convinced us, however, that too many assumptions would be involved in respect of transmissions of filters and absorptions of solutions under investigation to make this worth while.

Experimental

The arrangement of apparatus used was essentially similar to that described by Allmand (*loc. cit.*) and by Franklin, Maddison and Reeve² in Part II of this series. It consisted of a Hilger Monochromatic Illuminator for the Ultra-Violet, with a water-cooled shutter before the collimator slit, and provided at the telescope slit with a Hilger linear thermopile, which was connected to a Paschen galvanometer. The setting up of the apparatus had, however, been greatly improved, particularly with regard to the Paschen galvanometer, which now rested upon a concrete block, weighing nearly a ton, and standing upon a mound of loose earth in a pit, with no contact with the floor of the building. The shielding was the same as that described by Franklin (*loc. cit.*) but as all work was carried out at night, when traffic disturbances were at a minimum, the galvanometer was much steadier. Indeed, an unusual combination of circumstances gave perfect steadiness on one or two nights, enabling small readings to be made with great accuracy. A new suspension had been fitted to the galvanometer, giving about twice the sensitivity previously obtainable.

The installation of a Tirrill regulated motor-generator also enabled a constant voltage supply (110 volts) to be maintained.

¹ J. Chem. Soc., 107, 682 (1915).

² J. Phys. Chem., 29, 714 (1925).

The worst difficulties lay with the lamp itself. This was burnt for the main determinations at 2.42 amps, 29.5 volts, as these were the most stable conditions. It was found that the lamp frequently deposited thin films of mercury on the glass, thus changing the energy distribution, that it frequently went out, and that as it had to be burnt close to the shutter, in order to get as high an intensity as possible, the slightest change in position caused a disproportionately large change in the intensity of any line being examined. Hence the method was adopted of first examining each line at 1-2 $\mu\mu$ intervals¹, and then comparing the deflections given by the peaks of the various lines with that given by one line (436 $\mu\mu$) which was taken as standard. As many lines as possible were thus compared in each position, and the comparison made complete by bringing all the values to a common basis of 436 $\mu\mu$ = 100 mm. Each line was examined a number of times.

Finally an attempt was made to examine variation of distribution with current density. This was not very successful, owing to the limited stability of the lamp, but a few results are given.

The number of deflections measured for each line in each comparison varied from six to twenty. Under the best conditions it was possible to repeat a reading amounting to a few millimetres six times or more with less than .5 mm. difference. The maximum deflection obtained in any case was 80 mm.

One of us (H. N. R.) in collaboration with D. W. G. Style, has recently published in this series² an account of reflection losses in the spectrometer used, and the results given in Tables I and II are corrected by the factors in that paper.

Results

Taking 436 $\mu\mu$ as 100 mm., the following peak comparisons were obtained:—

| | | | | | | | | |
|--------------|----|-----|-----|----|-----|-----|----|----|
| 579 $\mu\mu$ | 16 | 16 | 38 | 47 | 37 | 36 | | |
| 546 | 97 | 104 | 126 | 93 | 102 | 115 | | |
| 405 | 64 | 72 | 69 | 68 | 71 | 71 | 79 | 69 |
| 365 | 30 | 30 | 31 | 33 | 35 | | | |
| 313 | 18 | 20 | | | | | | |
| 303 | 2 | | | | | | | |

Mean values are given in Table I (corrected).

The deflections obtained in the various portions of each wave-band were then compared with these peak values, and the results plotted in a graph (Fig. 1). From the graph the area of the diagram of each line was found, and this divided by $d\lambda$ (the wave length range included by the telescope slit at this wave length), should give the true energy content of each line (cf. Franklin, etc.: *op. cit.*, 716). The results are given in Col. 3 of Table I, and it will be seen that they closely correspond with the peak deflections given above.

¹ See Reeve: *J. Phys. Chem.*, 29, 40 (1925).

² *J. Phys. Chem.*, 32, 861 (1928).

In Col. 4 are given the results of Allmand, for comparison. These have also been corrected for reflection losses in the spectrometer, as this was an instrument of the same make, and probably the mirror was similar. In any case, the corrections are very small.

In Col. 5 are given, for comparison, figures for one of the quartz mercury lamps which have been examined in this laboratory.

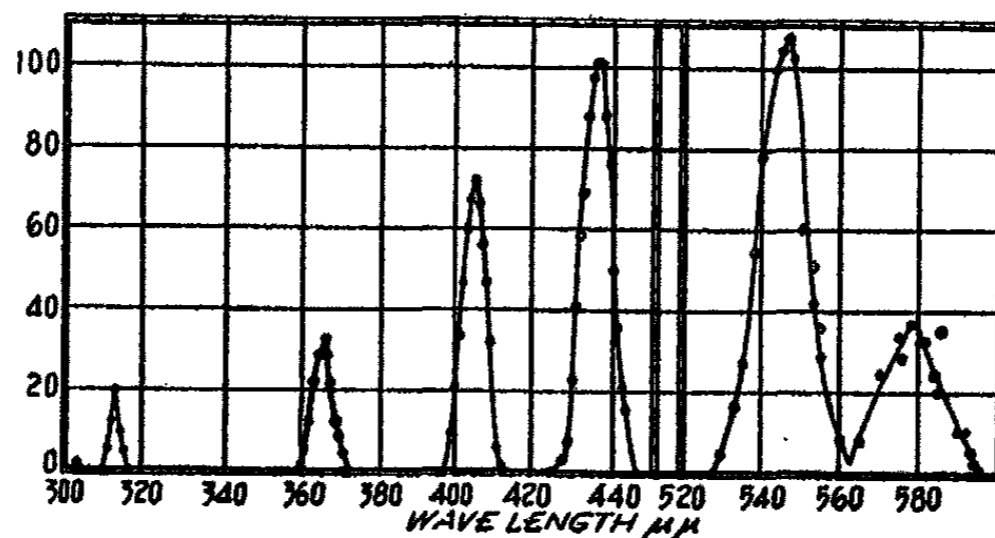


FIG. 1
The Energy Distribution of the Uviol Lamp burning
at 29.5 volts, 2.42 amps.

TABLE I

| Wave-length | Peak comparisons | Area $d\lambda$ | Allmand's figures | Quartz mercury lamp |
|--------------|------------------|-----------------|-------------------|---------------------|
| 579 $\mu\mu$ | 36 | 34 | 27 | 115 |
| 546 | 106 | 99 | 72 | 110 |
| 436 | 100 | 100 | 100 | 100 |
| 405 | 71 | 76 | 57 | 46 |
| 365 | 32 | 33 | 42 | 146 |
| 313 | 20 | 16 | 18 | 76 |
| 303 | 2 | | | 34 |

These results are at 2.42 amps. and 29.5 volts, except Col. 4 (3.2 amps. and 34 volts.). The effect of change of amperage is shown in Table II. (corrected).

TABLE II

| Wave-length | Peak Comparisons | | Wave-length | Peak Comparisons | |
|--------------|------------------|----------------|-------------|------------------|----------------|
| | 1.5 A. 30 V. | 3.5 A. 30.5 V. | | 1.5 A. 30 V. | 3.5 A. 30.5 V. |
| 579 $\mu\mu$ | 29 | 37 | 405 | 68 | |
| 546 | 93 | 108 | 365 | 27 | 31 |
| 436 | 100 | 100 | | | |

It will be noticed that there is practically no change in peak values when the current is raised from 2.42 to 3.5 amps. This agrees with Allmand's results.

Summary

The energy distribution of the Uviol Lamp has been examined, and the results compared with earlier work and with the energy distribution of the Quartz Mercury Lamp.

The authors wish to express their thanks to Professor A. J. Allmand for suggesting this work, and for his continual help and encouragement.

One of us (E. B.) also wishes to acknowledge a grant from the Board of Scientific and Industrial Research whilst a Student in Training.

*The University of London,
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March 16, 1928.*

SOME PHYSICAL PROPERTIES OF PHENOL IN BENZENE*

BY LLOYD E. SWEARINGEN

Introduction

In this laboratory work is being conducted on the physical properties of various types of solutions. In a recent paper¹ some data on the physical properties of aqueous hydroxy-benzene solutions were presented. The surface tensions of solutions of the same concentration of hydroxy-benzenes were found to vary considerably with the number and position of the (OH) groups in the benzene ring. The other physical properties investigated were not influenced in any striking manner. As the number of (OH) groups in the benzene ring increased, the hydroxy-benzenes became less effective in lowering the surface tension of water. The following arrangement represents the order of decreasing ability to lower the surface tension of water; Phenol > Catechol > Resorcinol > Hydroquinone > Pyrogallol. This same order is shown by the data of Harkins and Grafton.²

This order of effectiveness in lowering the surface tension of water might be expected and predicted from the nature of the substances concerned. The magnitude of the di-electric constant may be at least taken as a qualitative measure of the degree of polarity of a compound. The hydroxyl group is known to be a polar group and its polar influence on the benzene ring may be seen by comparing the di-electric constant of benzene (2.27), with that of phenol (9.7). It does not necessarily follow that the introduction of additional (OH) groups will render the molecule more polar, since the polarity of a molecule and its symmetry are intimately related. The influence of symmetry on polarity may be illustrated by the following data³

| Di-electric Constant | | Di-electric Constant | |
|-----------------------------------------------------------|-------|-------------------------|------|
| CH ₃ NO ₂ | 40.00 | CHCl ₃ | 5.14 |
| C(NO ₂) ₄ | 2.10 | CCl ₄ | 2.24 |
| Di-electric Constant | | | |
| C ₆ H ₅ Br..... | | 9.82 | |
| C ₆ H ₄ Br ₂ (meta)..... | | 8.81 | |
| C ₆ H ₄ Br ₂ (para)..... | | 4.57 | |

Nitro methane shows a moderately high degree of polarity, as indicated by the di-electric constant. When more nitro groups are introduced, the arrangement becomes more symmetrical and a corresponding decrease in polarity is observed. In the case of chloroform and carbon tetrachloride,

*Contribution from the Chemical Laboratory, University of Oklahoma.

¹ Swearingen: J. Phys. Chem., 32, 785 (1928).

² J. Am. Chem. Soc., 47, 1329 (1925).

³ Landolt-Börnstein "Tabellen" (1905).

the more symmetrical arrangement of the latter molecule is very probably responsible for the difference in polarity, as indicated by the difference in the dielectric constants. The dependence of polarity on symmetry is also illustrated by the brom-benzenes.

In the case of the di- and tri-hydroxybenzenes, we should expect to find the polarity of the molecule decreasing with increasing number of (OH) groups, if this increased number of groups produces a more symmetrical molecule. This decreased polarity should be manifested by a decrease in the ability of this molecule to effect such properties as are determined or influenced by inter-molecular attraction. This conclusion is in harmony with the data presented in the previous paper.

In the present paper, this work has been extended to the hydroxybenzene-benzene systems, where benzene, unlike water, has a low degree of polarity. Such properties of these systems, that are influenced by polarity, should be effected in a very different manner from the corresponding effects observed with aqueous hydroxybenzene systems.

Experimental

Material. Phenol. Merck and Company. "Absolute Phenol." C.P. Samples of this phenol were purified by repeated fractional crystallization. The transparent crystals were stored in glass containers in a large desiccator, over concentrated sulphuric acid.

Benzol. Merck and Company. C.P. Crystallizable Benzol. This benzol was frozen and purified in a manner similar to that used for the phenol.

The catechol, hydroquinone and pyrogallol were Merck and Company products of highest purity and were used without any additional treatment.

The resorcinol was furnished by the Mallinckrodt Chemical Company, C.P. quality, free from di-resorcin, phenol and acid. This sample was used without additional treatment.

The phloroglucinol was furnished by the Eastman Kodak Company and was used without additional treatment.

Procedure. Solutions of the phenols in benzene were prepared by weighing out the phenol samples in ground-glass stoppered flasks and then adding the desired amount of benzene from calibrated pipettes. Solutions were prepared in which the mole fractions of the phenol ranged from 0.083 to 0.786. Due to the small solubility of the di- and tri-hydroxybenzenes in benzene, a single saturated solution was prepared in each case.

The density, viscosity and surface tension of the different phenol-benzene mixtures were determined. Only surface tension data on the di- and tri-hydroxybenzenes were determined. These solutions were so dilute that their viscosities and densities were practically the same as these values for pure benzene.

The densities were determined in duplicate at 25°C with a Geissler pycnometer. The average of the two determinations is recorded. The maximum variation between the two values was eight units in the fourth

decimal place. Duplicate determinations with different pycnometers showed that the figure in the fourth place was reliable. A consideration of the various factors influencing the determination showed this place to be about the limit of accuracy. All densities have been referred to that of water at 4°C.

The viscosities were determined at 25° with a modified type of Ostwald-Poiseuille viscometer. Two different viscometers were used, one with a fine capillary for the mixtures of lower viscosity; the other with a larger capillary for the more viscous mixtures. The time of outflow was measured by two stop watches which recorded time to fifths of seconds. The data in all cases are reproducible to within 0.6%. The averages of four best determinations are recorded in each case.

The surface tension measurements were made at 25°C with a du Noüy tensimeter. The instrument was calibrated with both water and benzene at 25°C. All glassware was carefully cleaned and flamed before use. The thermostat was maintained constant to within 0.1°C. The results were easily reproducible with a high degree of accuracy.

Since some of the materials used in these experiments are markedly affected by moisture and oxygen, precaution was taken wherever possible to displace air with dry nitrogen.

Results

Due to the large difference in the composition of the solutions, the data for the phenol-benzene mixtures have been tabulated separately from the di- and tri-hydroxybenzene data.

TABLE I

| Sample No. | Mole Fraction Phenol | Phenol-Benzene Mixtures | | | |
|------------|----------------------|------------------------------------------------------|-----------------------------------------|----------------------------------------------------------|----------------------------------------------|
| | | Density $D_{4^{\circ}\text{C}}^{25^{\circ}\text{C}}$ | Relative Viscosity 25°C | Absolute Viscosity $\times 10^{-3}$ 25°C | Surface Tension (Dynes) 25°C |
| 0 | 0.000 | 0.87362 | 1.000 | 5.578* | 27.263** |
| 1 | 0.083 | 0.89112 | 1.145 | 6.592 | 27.375 |
| 2 | 0.181 | 0.9118 | 1.479 | 8.516 | 27.880 |
| 3 | 0.239 | 0.9236 | 1.601 | 9.218 | 28.183 |
| 4 | 0.279 | 0.9313 | 1.801 | 10.370 | 28.440 |
| 5 | 0.370 | 0.9477 | 2.010 | 11.573 | 28.867 |
| 6 | 0.478 | 0.9710 | 2.945 | 16.957 | 29.891 |
| 7 | 0.522 | 0.9794 | 3.212 | 18.494 | 30.302 |
| 8 | 0.619 | 0.9988 | 4.412 | 25.404 | 31.418 |
| 9 | 0.658 | 1.0065 | 4.833 | 27.828 | 32.220 |
| 10 | 0.692 | 1.0147 | 5.509 | 31.720 | 32.776 |
| 11 | 0.762 | 1.0271 | 6.923 | 39.360 | 33.866 |
| 12 | 0.786 | 1.0340 | 7.683 | 44.239 | 34.211 |
| 13*** | (1.000) | (1.0775) | () | (72.500) | (39.300) |

* Viscosity of pure benzene at 25° C. from Fischler: Z. Elektrochemie, 128, 19 (1913).

** Surface tension of pure benzene at 25°C, from Morgan and Egloff: J. Am. Chem. Soc., 39, 2151 (1917).

*** Data for pure phenol extrapolated from data.

TABLE II
Benzene-Di- and Tri-hydroxybenzene Mixtures

| Sample | Concentration of Saturated Solution at 25°C, Grams/1000 grams C ₆ H ₆ | Surface Tension. (Dynes) 25°C |
|----------------|---------------------------------------------------------------------------------------------|-------------------------------|
| Catechol | 1.5521 | 26.95 |
| Resorcinol | 4.2094 | 26.92 |
| Hydroquinone | 0.4010 | 26.85 |
| Pyrogallol | 0.8340 | 26.85 |
| Phloroglucinol | 1.0008 | 26.85 |

TABLE III
Apparent Molal Volume of Phenol in Benzene, 25°C

| Density | Mole Fraction Phenol | Moles of Phenol in 1000 grams of Benzene | Grams of Phenol per 1000 grams C ₆ H ₆ | Volume of Solution containing 1000 grams of Benzene | The Apparent Molal Volume of Phenol in Benzene |
|---------|----------------------|------------------------------------------|--------------------------------------------------------------|-----------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|
| D | X ₂ | N ₂ | G ₂ | V | O |
| 0.8736 | 0.000 | 0.0000 | 0.000 | 1144.66 | 00.00 |
| 0.8912 | 0.083 | 1.1794 | 110.875 | 1246.53 | 86.70 |
| 0.9117 | 0.181 | 2.8596 | 270.651 | 1393.57 | 87.04 |
| 0.9236 | 0.239 | 4.0110 | 379.668 | 1493.81 | 87.04 |
| 0.9313 | 0.279 | 4.9562 | 467.842 | 1576.10 | 87.05 |
| 0.9477 | 0.370 | 7.5380 | 678.563 | 1771.29 | 83.12 |
| 0.9710 | 0.478 | 11.7104 | 1100.046 | 2162.67 | 86.98 |
| 0.9794 | 0.522 | 13.9465 | 1309.820 | 2358.33 | 87.02 |
| 0.9988 | 0.619 | 20.7468 | 1949.170 | 2952.74 | 87.14 |
| 1.0065 | 0.658 | 24.6887 | 2319.732 | 3298.16 | 87.22 |
| 1.0147 | 0.692 | 28.7920 | 2702.743 | 3649.17 | 86.98 |
| 1.0271 | 0.762 | 40.9174 | 3846.473 | 4718.55 | 87.34 |
| 1.0340 | 0.786 | 53.9445 | 5086.181 | 5883.21 | 87.84 |
| | | | | | Average (excluding No. 6).....87.11 |
| | | | | | Molal volume of solid phenol at 20°C calculated from its density...87.76 |
| | | | | | Molal volume of solid phenol at 25°C calculated from the density of phenol obtained by extrapolating the densities of the phenol-benzene mixtures.....87.31 |

Discussion

The density of the phenol-benzene mixtures is shown in Fig. 1 as a function of the concentration of the phenol in the mixture. The relation is a linear one, the density-mole fraction curve being for all practical purposes a straight line. Extrapolation of this data gives a value of 1.0775 for the density of phenol at the point where its mole fraction is unity. Dunstan, Hilditch and Thole¹ report 1.070 for the density of phenol at 25°C. Extrapolation of the data of Morgan and Egloff² gives approximately 1.0708 for the density of phenol at 25°C.

¹ J. Chem. Soc., 103, 133 (1913).

² J. Am. Chem. Soc., 38, 844 (1916).

The apparent molal volume of phenol in benzene at 25°C was determined from the known concentrations of the mixtures and their determined densities.

If N_2 represents the number of moles of phenol in 1000 grams of benzene, G_2 the number of grams of phenol in 1000 grams of benzene and V the volume of the solution containing 1000 grams of benzene, then the apparent molal volume of the phenol in the mixture and these quantities are related as follows:

$$\Phi = \frac{V - V_0}{N_2}$$

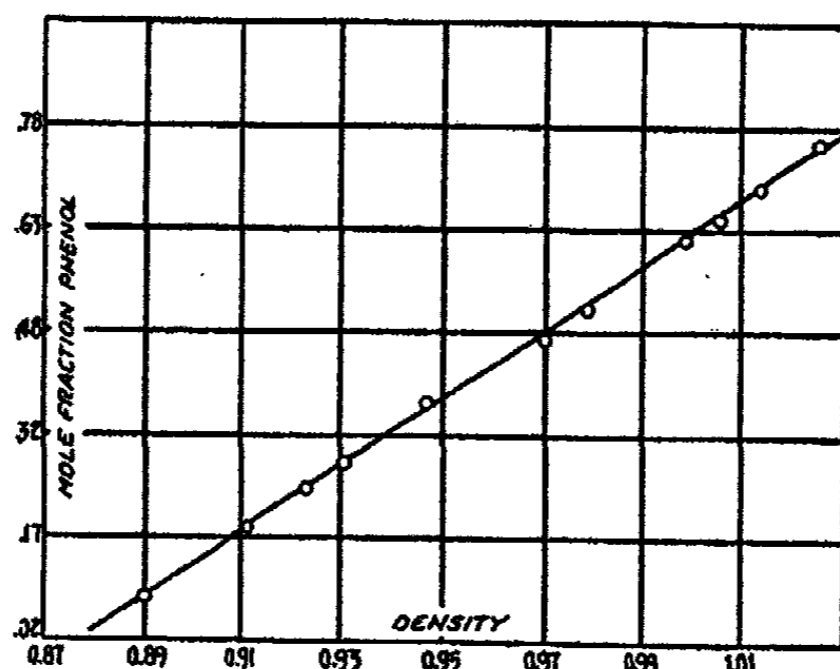


FIG. 1

V is given by the equation $V = (G_2 + 1000)/D$, where D is the density of the mixture at 25°C. V_0 is given by the equation $V_0 = 1000/D_0$, where D_0 is the density of the benzene at 25°C and was taken 0.87362. This gives a value of 1144.66 for the value of V_0 , the volume of 1000 grams of benzene at 25°C.

According to Dunstan viscosity-concentration curves may be grouped into three classes, according to whether the curve approximates a straight line, exhibits a maximum, or a minimum. The first class includes mixtures of those substances which are chemically indifferent toward each other, the molecules of which are not associated. The second class includes those substances which are supposed to react chemically with each other. The third class is composed of those substances which do not react chemically with each other but do contain associated molecules, the low viscosity being due to the dissociation of the complex.

The viscosity-composition curve for the phenol-benzene mixtures shown in Fig. 2 exhibits a minimum and apparently belong to Dunstan's third class of mixtures. Phenol, in the liquid state must consist largely of associated molecules. The dissociation of the complex into the simpler forms will have taken place to a greater extent in dilute than in concentrated solutions. Reference to Fig. 2 shows the minimum point to come at the smaller phenol concentrations.

The viscosity of pure phenol at 25°C obtained by extrapolation from Fig. 2 gives a value of 0.0725 absolute units. Bramley¹ obtains a value of 0.1104 absolute units for the viscosity of phenol at 20°C. Dunstan reports a value of 0.085 for the absolute viscosity of phenol at 25°C.

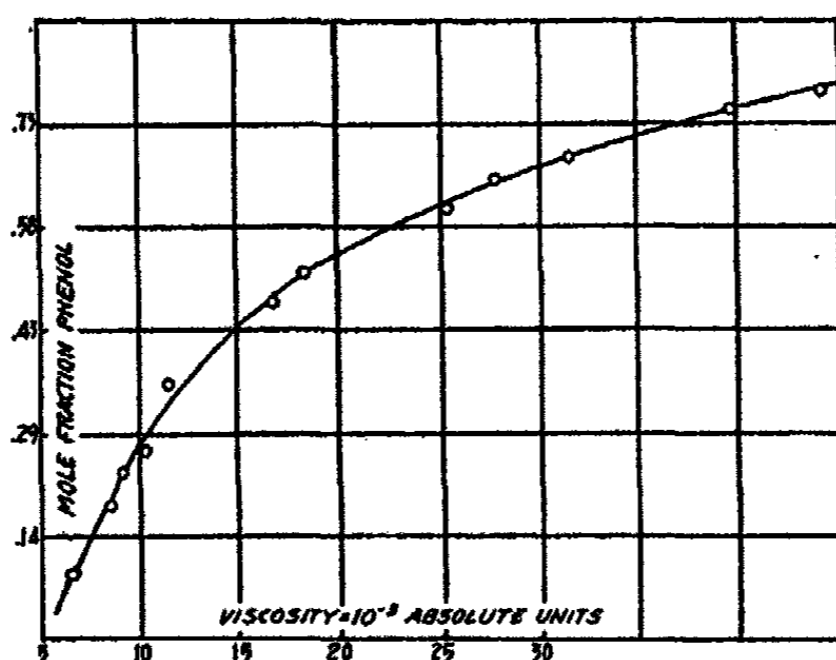


FIG. 2

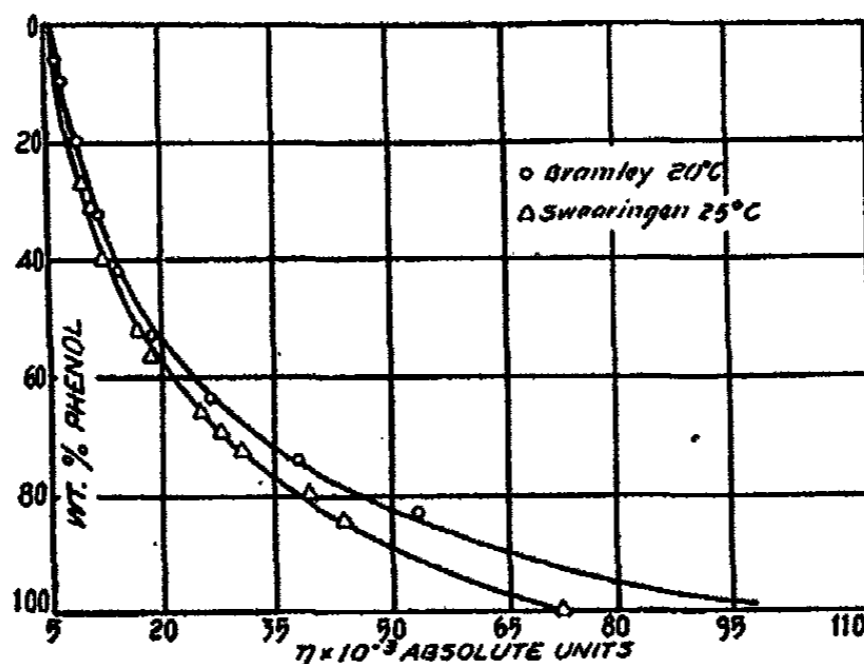


FIG. 3

Bramley has determined the densities and viscosities of phenol in benzene for various concentrations of phenol at 20°C. For comparison the data given in Table I have been converted into weight percent and these data together with the data of Bramley have been reproduced in Fig. 3. Good agreement is shown at the lower phenol concentrations. At the higher concentrations, the curves have the same general form, but there is a considerable displacement of Bramley's data in the direction of greater viscosity at

¹ J. Chem. Soc., 109, 10 (1916).

the higher concentrations of phenol. This is to be expected from the temperature differences.

The surface tension-composition data are shown graphically in Fig. 4. There is a marked similarity between the surface tension composition and the viscosity-composition curves. The latter are much more convex toward the concentration axis than the former. The rise in surface tension with concentration of phenol is much more gradual than the change in viscosity with concentration of phenol. The minimum is located more symmetrically with respect to the surface tension of the pure components. Extrapolated

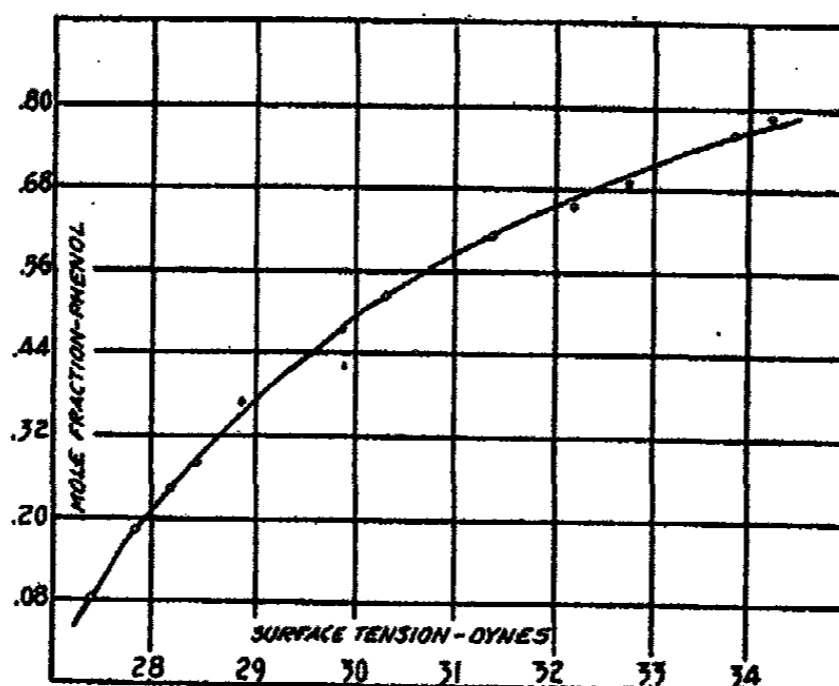


FIG. 4

data gives the value of the surface tension of pure phenol to be 39.3 dynes at 25°C. Interpolated data of Morgan and Egloff show this value to be approximately 39.07 dynes.

Saturated solutions of the di- and tri-hydroxybenzenes in benzene (Table II) show a smaller surface tension value than pure benzene. The departures in each case from the surface tension value of pure benzene is but slight.

When phenol is dissolved in water, there is a marked lowering of the surface tension of the solution over that of pure water. Phenol is said to lower the surface tension of water. Water molecules are highly polar and a considerable amount of work will be required to bring water molecules into the surface when the surface is extended. Phenol molecules, on the other hand, being less polar are brought into the surface with a smaller expenditure of energy. The presence of the phenol molecules in the surface, due to their lower surface tension, tends to decrease the surface tension of the mixture of molecules to a smaller value than that for a pure water surface. Consequently, when the surface of a phenol-water mixture is extended, phenol molecules will enter the surface layer to a greater extent than the water molecules will. This will bring about a concentration of phenol molecules in the interface and the phenol is said to be adsorbed in the interface.

When phenol, with its moderate polarity is dissolved in benzene, which has a very low degree of polarity, the phenol operates to raise the surface tension of the solution over that of pure benzene. Benzene molecules, with their lower polarity are more easily brought into the interface than phenol molecules. The extension of a phenol-benzene surface, the entrance of benzene molecules into the surface layer will be favored over the entrance of phenol molecules. Some phenol molecules will however enter the surface layer, even at low concentrations of phenol. As a result of their entrance into the surface layer, the surface tension of the mixed surface will be somewhat greater than that of the pure benzene surface. The concentration of the phenol molecules in the surface will increase as the concentration of the phenol increases in the bulk of the solution. As a result of this increasing phenol concentration in the interface, the surface tension of the solution will gradually increase. The concentration of the phenol molecules in the interface will always be less than the concentration of phenol in the bulk of the solution, as long as there is any benzene present. This may be described as a case of negative adsorption of phenol or positive adsorption of benzene in the interfacial layer.

Summary

1. The densities of phenol-benzene mixtures have been determined for various concentrations of phenol, at 25°C. The relation between density and concentration is a linear one.
2. From the observed densities and the known concentration of the mixtures, the partial molal volume of phenol in the various mixtures has been calculated. The values obtained have been practically constant, indicating that phenol and benzene form essentially an ideal solution. The average molal volume of the phenol in the mixture corresponds closely with the molal volume of phenol as calculated from the density and molecular weight.
3. The viscosities of phenol-benzene mixtures have been measured. A decided minimum in the viscosity-composition curve has been found, the minimum point being very pronounced in the more dilute phenol mixtures. This behavior has been explained on the basis of associated phenol molecules in the more concentrated solutions, which dissociate in the more dilute solutions to give this abnormal effect.
4. The surface tensions of the various phenol-benzene mixtures have been determined. A minimum has also been found in the surface tension-composition curves. The surface tension effects noted are explainable on the basis of negative adsorption of the phenol at the phenol-benzene interface.

Norman, Oklahoma.

PHOTOTROPIC COMPOUNDS OF MERCURY

BY S. V. RAGHAVA RAO AND H. E. WATSON

It has previously been shown by one of us¹ that the yellow compound HS.Hg.CNS prepared by the action of thio-urea and ammonium sulphocyanide upon a concentrated solution of mercuric chloride in acetic acid in presence of an oxidising agent is very rapidly turned black by exposure to light and regains its original colour after standing for a short time in the dark or on heating. The compounds Cl.Hg.CNS, Br.Hg.CNS, and I.Hg.CNS, the first of which was originally prepared by McMurthy² have also been shown to possess similar properties.

The corresponding cyanates and selenocyanides have now been prepared, as well as a number of double sulphides, and the phototropic properties of the more sensitive compounds have been examined in a quantitative manner. Attempts to prepare similar tellurium compounds have not been successful.

Experimental

These compounds are all insoluble or very slightly soluble in water and accurate analytical results were somewhat difficult to obtain. The figures given are sufficient to identify the compounds with the suggested formulae but are not accurate enough to indicate the presence of small quantities of impurities. As it was considered possible that the phototropic properties might be considerably modified by traces of foreign matter a comparison was made in several cases between preparations of the same compound made at different times and by alternative methods, but the differences observed were always small and hardly beyond the limit of experimental error.

In conducting the analysis, mercury was estimated as sulphide by Volhard's method after solution of the compound in aqua regia. Halogens were determined by decomposing the compounds with a large excess of fusion mixture, sulphur by heating with sodium carbonate and potassium nitrate and estimation as barium sulphate, and selenium by solution in aqua regia followed by evaporation with hydrogen chloride and precipitation with sulphur dioxide. When selenium was present, mercury was estimated as mercurous chloride.

Cyanates

The compounds HS.Hg.CNO and HO.Hg.CNO could not be obtained by treating a mercury salt with ammonium cyanate and thiourea or urea. The halides Cl.Hg.CNO and Br.Hg.CNO were prepared by boiling together equimolecular proportions of mercuric cyanate and the mercury halide for some time and filtering. The complex salts crystallised out. The

¹ Nature, 111, 775 (1923).

² J. Chem. Soc., 55, 50 (1889).

iodine compound could not be produced in this way but was obtained as an insoluble residue when mercuric cyanate was boiled with a slight excess of potassium iodide, the yield being quantitative.

The bromine and iodine compounds were also formed by the action of an alcoholic solution of the halogen upon mercurous cyanate.

Chloro-mercuric cyanate is a pale brown substance. It turns dark brown in about half an hour in diffused daylight and regains its original colour after keeping it in the dark for two days. Analysis gave Hg, 72.3; Cl, 12.7: Cl.Hg.CNO requires Hg, 72.0; Cl, 12.8.

Bromo-mercuric cyanate is yellow and darkens more rapidly than the chlorocompound. The time for reversal is about the same. Analysis gave Hg, 62.9; Br, 25.1: Br.Hg.CNO requires Hg, 62.1; Br, 24.8.

Iodo-mercuric cyanate has a bright golden yellow colour and blackens completely in about 3 minutes in diffused daylight. The reversal takes place slightly faster than in the two preceding cases. Analysis gave Hg, 53.6; I, 34.2: I.Hg.CNO requires Hg, 54.2; I, 34.4.

To avoid loss of iodine during analysis, decomposition of this compound was effected by gentle heating with potassium hydroxide.

Selenocyanides

The compounds HS.Hg.CNSe and HSe.Hg.CNSe as also the halogen double salts were obtained without difficulty. The compound HSe.Hg.CNSe is not phototropic.

Chloro-mercuric selenocyanide has been prepared by Rosenheim and Pritz¹ by adding potassium selenocyanide to a concentrated solution of mercuric chloride. It can also be prepared by treating mercuric selenocyanide with a dilute solution of potassium chloride. It is very feebly phototropic. Analysis gave Hg, 59.2; Se, 23.8; Cl, 10.1: Cl.Hg.CNSe requires Hg, 58.7; Se, 23.3; Cl, 10.4.

For analysis the compound was decomposed with potassium hydroxide.

Bromo-mercuric selenocyanide was prepared by treating mercuric selenocyanide with a dilute solution of potassium bromide. It is a very fine powder and blackens in about 2 minutes in diffused daylight. The original colour returns in about 24 hours at room temperature (30°). Analysis gave Hg, 51.5; Se, 20.3; Br, 20.8: Br.Hg.CNSe requires Hg, 51.9; Se, 20.6; Br, 20.8.

Iodo-mercuric selenocyanide prepared in an analogous manner is an orange powder. It darkens in less than 2 minutes. The reversal is much slower than with the bromine compound. Analysis gave Hg, 45.7; Se, 18.2; I, 29.1: I.Hg.CNSe requires Hg, 46.2; Se, 18.3; I, 29.3.

Hydrosulpho-mercuric selenocyanide is formed as a light brown substance when a slow current of hydrogen sulphide is passed through mercuric selenocyanide suspended in water. It is very feebly phototropic taking an hour and a half to darken in diffused daylight. It returns to its original colour in the dark in about 3 days. Analysis gave Hg, 60.2; Se, 23.9; S, 9.5: HS.Hg.CNSe requires Hg, 59.2; Se, 23.4; S, 9.4.

¹ Z. anorg. Chem., 63, 275 (1909).

Hydroseleno-mercuric selenocyanide is a brown compound which appears to be HSe.Hg.CNSe from its method of formation (i.e. by passing H_2Se into $\text{Hg}(\text{CNSe})_2$ suspended in water) and is not phototropic.

Hydroseleno-mercuric sulphocyanide similarly formed as a grey powder on passing H_2Se into $\text{Hg}(\text{CNS})_2$ suspended in water is also not phototropic.

Double Sulphides of Mercury

The two compounds $\text{Hg}_3\text{S}_2\text{Br}_2$ and $\text{Hg}_3\text{S}_2\text{I}_2$ first prepared by Franceschi¹ have been found to be phototropic by Varahalu.² The corresponding chloro-, sulphocyno- and selenocyno-compounds have been prepared. An attempt to prepare the corresponding cyanide and cyanate ended in failure.

Trimeric-disulpho-dichloride has been obtained as a white crystalline substance by adding potassium chloride solution to a solution of freshly precipitated mercuric sulphide in mercuric acetate. It has also been obtained by adding hydrogen sulphide solution to mercuric chloride solution acidified with hydrogen chloride.³ It turns black in about 10 minutes in diffused daylight. Reversal takes two days at room temperature.

Trimeric-disulpho-disulphocyanide is prepared from mercuric sulphide dissolved in mercuric acetate by precipitation with potassium sulphocyanide solution. It is yellow at first but becomes slightly greenish. It darkens in diffused daylight in about 2 to 3 minutes and regains its original colour in the dark after two days. Analysis gave Hg, 76.6; S, 16.5; $\text{Hg}_3\text{S}_2(\text{CNS})_2$ requires Hg, 77.0; S, 16.4.

Trimeric-disulpho-diselenocyanide is prepared in an analogous manner by using potassium selenocyanide solution for precipitation. It is a brown solid which turns crimson on exposure to light for about six minutes. It regains its original colour in about 40 hours in the dark.

For determination of sulphur the substance was fused with a mixture of potassium nitrate and sodium carbonate; the fusion extract was repeatedly boiled with concentrated hydrogen chloride in which selenium was precipitated and filtered. From the filtrate the sulphate was precipitated in the usual way. Analysis gave Hg, 68.4; Se, 17.9; S, 7.2; $\text{Hg}_3\text{S}_2(\text{CNSe})_2$ requires Hg, 68.7; Se, 18.1; S, 7.3.

Double Selenides and Oxides

The selenides corresponding with the halogen double sulphides have also been prepared and examined together with one oxygen compound $\text{Hg}_3\text{O}_2(\text{CNS})_2$.

Trimeric-diseleno-dichloride is formed as a white precipitate when a slow stream of hydrogen selenide is passed into an aqueous solution of mercuric chloride⁴. It is feebly phototropic, taking nearly two hours to darken in diffused daylight. Reversal takes about 2 days at room temperature.

¹ Boll. chim. farm., 55, 481 (1916).

² J. Sci. Ass. Vizianagram, 1, 101 (1924).

³ Rose and Palm; Russ. Pharm. Ztg., 1862, 120.

⁴ Uelsmann; Jahresber., 1860, 92.

Trimeric-mercuric-diseleno-dibromide is obtained as a pale yellow substance by passing hydrogen selenide into a solution of mercuric bromide. It takes 40 to 50 minutes to darken completely in diffused daylight, while in the direct sun the change is brought about in 8 to 10 minutes. The reverse change takes about 36 hours. Analysis gave Hg, 65.4; Br, 17.6; Se, 17.2: $\text{Hg}_3\text{Se}_2\text{Br}_2$ requires Hg, 65.4; Br, 17.4; Se, 17.2.

Trimeric-mercuric-diseleno-diiodide is obtained as a light brown substance by treating either trimeric-mercuric-diseleno-dichloride or the dibromide with excess of potassium iodide solution. It darkens in less than 5 minutes in diffused daylight and takes the same time as the dibromide to recover. Analysis gave Hg, 59.6; I, 25.3; Se, 15.8: $\text{Hg}_3\text{Se}_2\text{I}_2$ requires Hg, 59.3; I, 25.0; Se, 15.6.

Trimeric-mercuric-dioxy-disulphocyanide is formed as a yellow powder when mercuric sulphocyanide is treated with ammonia. It is very feebly phototropic taking 3 to 4 hours to darken in sunlight. The recovery, however, is complete in three days. Analysis gave Hg, 80.5; S, 8.7: $\text{Hg}_3\text{O}_2(\text{CNS})_2$ requires Hg, 80.3; S, 8.5. No water was eliminated on decomposing the compound by heat.

Table I gives a list of these compounds and their properties.

TABLE I
Phototropic Mercury Compounds

| Substance | Colour | Darkening time, minutes | Time for recovery, days |
|------------------------------------------|---------------|-------------------------|-------------------------|
| Cl.Hg.CNO | Pale brown | 30 | 2 |
| Br.Hg.CNO | Pale yellow | 15 | 2 |
| I.Hg.CNO | Golden yellow | 3 | 1.5 |
| Cl.Hg.CNS | White | 20 | 2 |
| Br.Hg.CNS | White | 2 | 2 |
| I.Hg.CNS | Orange yellow | 1 | 1.5 |
| Cl.Hg.CNSe | Pale yellow | 20 | 1.5 |
| Br.Hg.CNSe | Yellow | 2 | 1 |
| I.Hg.CNSe | Orange | <2 | 1.5 |
| HS.Hg.CNS | Lemon yellow | <1 | 2 |
| HSe.Hg.CNS? | Grey | not ph. | |
| HS.Hg.CNSe | Pale brown | 90 | 3 |
| HSe.Hg.CNSe? | Brown | not ph. | |
| Hg.Cl ₂ , ₂ HgS | White | 10 | 2 |
| Hg.Br ₂ , ₂ HgS | Pale yellow | 3 | 2 |
| Hg.I ₂ , ₂ HgS | Orange yellow | <1 | 2 |
| Hg.Cl ₂ , ₂ HgSe | White | 120 | 2 |
| Hg.Br ₂ , ₂ HgSe | Pale yellow | 45 | 1.5 |
| Hg.I ₂ , ₂ HgSe | Pale brown | 5 | 1.5 |
| Hg(CNS) ₂ , ₂ HgO | Yellow | 200 | 3 |
| Hg(CNS) ₂ , ₂ HgS | Yellow green | 3 | 2 |
| Hg(CNSe) ₂ , ₂ HgS | Brown | 6 | 1.5 |

It is interesting to note that although the darkening times for these compounds vary through a very wide range, the times of recovery are all of the same order.

Spectroscopic Examination

The more active of these compounds have been exposed to light in a spectroscope in order to compare the effect of the different wave lengths. Similar experiments have been made by H. Stobbe¹ with the fulgides using a special spectroscope which gave very intense illumination. In the present case owing to the greater sensitivity of the compounds examined an ordinary spectroscope could be used.

The substance was mixed with sufficient 0.1 per cent solution of gelatine to enable it to flow freely, coated on a glass plate and dried in the dark. Strips of the plate were then exposed for varying times in the spectroscope to the light from a 100 c.p. pointolite lamp. For examination in the ultra-violet a quartz spectroscope was used with an iron arc as source of light, but this was somewhat difficult to keep constant in intensity and consequently most of the measurements were made in the visible region.

As the compounds under investigation regained their original colour in the dark, it was anticipated that exposure of the darkened substance to red light would have a bleaching effect and this was found to be the case, the general action of light being bleaching (of the substance after exposure to white light) in the red or infra-red, a neutral zone in the yellow or orange and darkening in the green and blue.

In order to preserve a permanent record of the appearance of the plates after exposure, they were illuminated with light of a wave-length which had no action upon them by means of filters and photographed upon a panchromatic plate.

Fig. 1A shows the curve obtained for the compound HS.Hg.CNS when the reciprocals of the times of exposure are plotted against the limits to which visible darkening extended after exposure. The portion of the curve below the zero line indicates that the previously exposed plate was bleached in the time noted. It will be seen that the curve has a flat top and very steep sides so that the chief sensitive region is distributed over a comparatively wide band of frequency but the limits are fairly sharply defined. This could be distinctly seen on the plates to which longer exposures had been given in which two dark zones were visible, the central darker one corresponding with the above limits.

The darkening in the ultra violet was apparently uniform and extended to the limit of transmission of the spectroscope. Similarly the bleaching effect had no evident maximum, and examination with a grating (for the loan of which we are greatly indebted to Dr. E. P. Metcalfe of the Central College, Bangalore) into the infra-red did not disclose the existence of a non-sensitive region.

¹ Ann., 359, 1 (1908).

Fig. 1 also shows sensitivity curves for seven other substances. They are all of a similar nature except the one for the compound $\text{Hg}_3\text{S}_2\text{Cl}_2$ which exhibits fairly uniform darkening in the blue and ultraviolet regions with a sharp cut off in the green, but no maximum. The exact shape shown for the curves on the blue side may be in some cases not quite correct owing to the absorption of the glass, although checked as accurately as possible with the quartz spectrograph. The limits of sensitiveness at the red end are however well defined and it will be noticed that the substitution of Cl by Br and Br by I

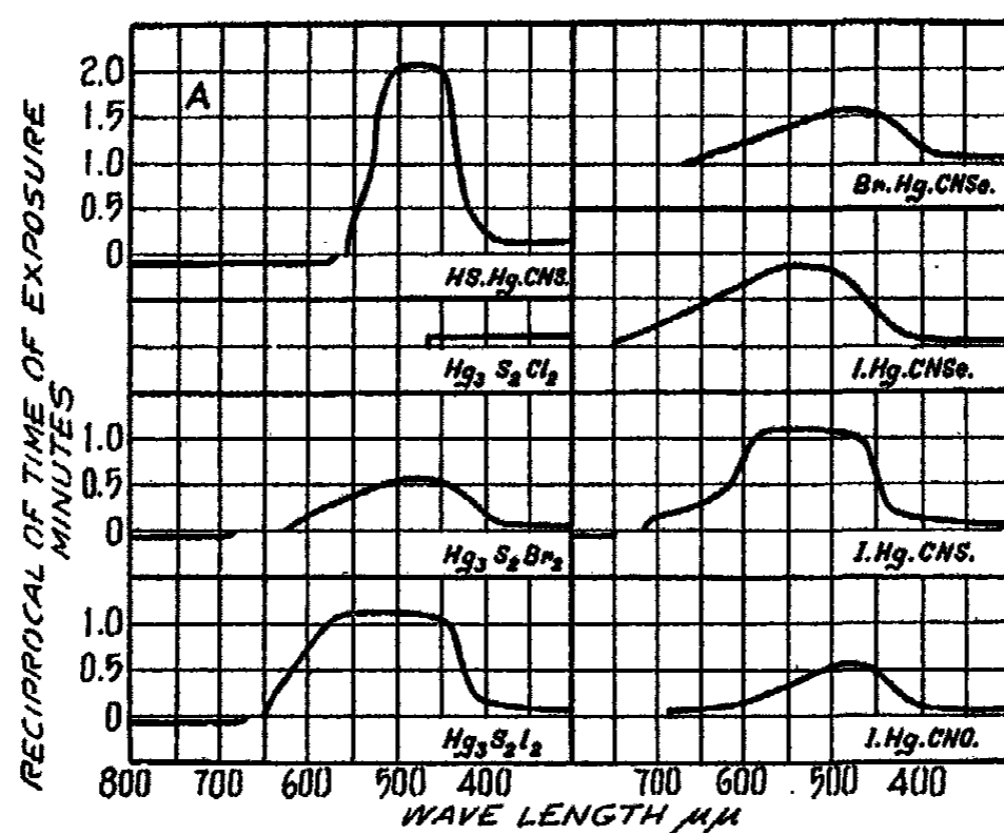


FIG. 1

in the series $\text{Hg}_3\text{S}_2\text{X}_2$ results in a shift of the maximum and of the excitation limit towards the red. A similar shift takes place on substitution of I for Br in the compound Br.Hg.CNSe , and also in the series I.Hg.CNO , I.Hg.CNS , I.Hg.CNSe .

The points at which reversal begins are also marked when they could be ascertained, but in several cases they were too far in the red to be detected. Some observations were also made with the compounds $\text{Hg}_3\text{S}_2(\text{CNS})_2$ and $\text{Hg}_3\text{S}_2(\text{CNSe})_2$. The region of maximum sensitiveness for the former extended from 4550–5000 A.U. thus coinciding nearly with that for the compound $\text{Hg}_3\text{S}_2\text{Br}_2$ but the sensitive region reached only to 5700 and reversal started at 6000 as compared with 6250 and 6850 for the bromine compound. The selenium compound had a wider maximum sensitiveness (4800–5575) further in the red than that of the sulphur compound and the sensitive region reached to 6350. Reversal could not be detected in the spectroscope.

Action of the Medium

It has been mentioned that gelatine was used to attach the varying compounds to the glass plates. Preliminary experiments were made to determine

the effect of this substance on the sensitiveness using the compound HS. Hg.CNS. Plates were coated with suspensions of the compound in gelatine solutions of different concentrations and exposed in the spectroscope for varying periods. About 1 gram of substance was mixed with 100 c.c. of gelatine solution so that in the case of a 1 per cent. solution the weight of gelatine amounted to 10 per cent. of the weight of the compound. Table II shows the region in which perceptible darkening occurred.

TABLE II

Effect of Concentration of Gelatine upon Sensitiveness of HS.Hg.CNS.

| Conc. of Gelatine | Region darkened (A.U.) in | | |
|-------------------|---------------------------|-----------|-----------|
| | 2 minutes | 4 minutes | 8 minutes |
| 0.23 | 4520-5340 | 4270-5570 | 4100-5630 |
| 0.47 | 4470-5340 | 4230-5570 | 4100-5630 |
| 0.93 | 4410-5410 | 4210-5640 | 4040-5640 |
| 1.86 | 4470-5340 | 4270-5580 | 4070-5630 |

The quantity of gelatine has thus a distinct influence upon the sensitiveness, there being a maximum at a concentration of about 10 per cent. of the weight of the substance.

It has been observed by M. L. Dey¹ that a gelatine emulsion of $Hg_3S_2I_2$ blackens more rapidly than the pure substance but he also states that the reverse change is completely inhibited. As this latter observation was not confirmed by our experiments it was decided to examine the phenomenon in somewhat greater detail.

Plates were coated with three different compounds with the addition of small quantities of binding agents and each set exposed to diffused daylight until the colouration reached a standard shade. The times taken to attain this colour were noted. The plates were then put in an electrically heated oven at either 50° or 70° for 45 or 35 minutes respectively and the extent to which bleaching had taken place at the end of the time was noted. The relative order of recovery could thus be judged. Table III shows the results of these experiments.

In the experiments marked (a) reversal was effected at 50° and in those marked (b) at 70°. As the order of reversal was the same at both temperatures in every case, only one set of figures has been given. There is no relation between the times (a) and (b) or for the figures which refer to different compounds. The only results which are comparable are those for the same substance with different media shown in one vertical column. From these it may be seen that the velocity of colouration depended in every case upon the medium only and that while agar agar, gelatine and collodion in the amounts employed exerted a marked accelerating influence, gum arabic produced a retardation. All the media had a retarding influence upon the reverse reaction.

¹ Nature, 112, 240 (1923).

TABLE III

Action of Different Media upon Sensitivity

| Medium | HS.Hg.CNS | | | I.Hg.CNS | | | Hg ₂ I ₂ | | |
|---------------------|----------------------------------------|----------------------|---|----------------------------------------|----------------------|---|---------------------------------------|----------------------|---|
| | Secs. re- quired for colouration | Order of reversal | | Secs. re- quired for colouration | Order of reversal | | Secs re- quired for colouration | Order of reversal | |
| | <i>a</i> | <i>b</i> | | <i>a</i> | <i>b</i> | | <i>a</i> | <i>b</i> | |
| Agar Agar 0.1% | 90 | 150 | 3 | 280 | 540 | 3 | 250 | 240 | 3 |
| Gelatine 0.1% | 120 | 200 | 5 | 300 | 600 | 3 | 270 | 260 | 5 |
| Collodion 0.06% | 155 | 255 | 3 | 330 | 660 | 2 | 280 | 270 | 3 |
| Nil | 180 | 300 | 1 | 360 | 720 | 1 | 300 | 285 | 1 |
| Gum arabic 0.13% | 230 | 420 | 2 | 390 | 810 | 3 | 340 | 330 | 2 |

Sensitisation by Means of Dyes

As all the substances examined showed marked differences of sensitivity to light of different wave-lengths it was considered probable that the position of the sensitive region would be altered by the action of dyes as it is in the case of the photographic plate.

In order to test this a series of experiments was made with the compound HS.Hg.CNS. Plates coated with this substance with a small quantity of gelatine as adhesive were dipped in dilute solutions (about 1 in 20,000) of various dyes for 1 minute and then dried. Experiments with erythrosin in which dye solutions of very different concentrations were used, indicated that the effect of concentration upon the sensitiveness was not appreciable provided that more than a certain minimum amount of dye-stuff was used. The plates were exposed to the light from a pointolite lamp in the spectro-scope as in the former experiments, both without previous exposure to light and after slight fogging in daylight.

In all cases the dyes had a distinct effect. The region in which darkening occurred was extended towards the red while the zone of reversal was also affected. The nature of these changes is shown in Fig. 2, the portion of the curve above the line indicating darkening and the portion below, bleaching. It is interesting to note that the two regions overlap. In the blue region it is possible even in the less sensitive parts to obtain practically complete blackening with sufficient exposure. Where the two curves overlap blackening is not so complete and only a well-darkened plate shows the bleaching effect. It is evident that in this case the velocities of the direct and reverse reactions are comparable so that an equilibrium is established.

An examination of the curves shows that the blue and green dyes sensitise furthest towards the red but that the sensitising effect of eosin and erythrosin is more marked.

An interesting phenomenon was noticed when these dyed plates were exposed to light of different wave lengths. The colour produced by light in the normal region of maximum sensitiveness (blue-green) differed distinctly in shade from the colour in the orange region which resulted from the presence of the dye. Without dye, there would have been a bleaching effect in this region. The difference was noticeable with all the dyes used but was most conspicuous in the case of eosin and erythrosin. The effect may be due to a difference in the state of molecular aggregation but no definite information on the subject is yet available.

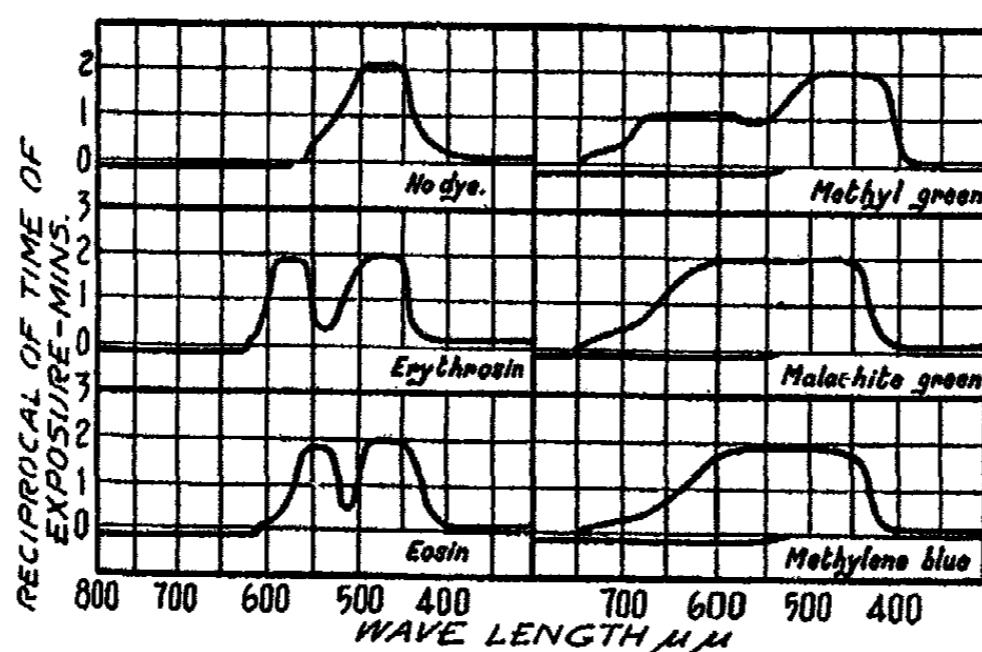


FIG. 2

A kindred effect was observed when a dyed plate previously exposed in the spectrograph was exposed to daylight. The unexposed portion darkened more rapidly than the part which had been exposed to red light so that after a short interval the former was actually darker than the latter. This appears to indicate that preliminary exposure to red light desensitises the material. The effect was similar when the second exposure was made through a blue screen.

Temperature Coefficients of Direct and Reverse Reaction Velocities

A number of measurements have been made with the object of determining as far as possible the temperature coefficients of the reactions in the light and in the dark. Two compounds HS.Hg.CNS and I.Hg.CNS were studied and the method adopted was to measure the time required to change from one tint to another under varying conditions. As it was not possible to use darkened specimens of the substances themselves for comparison purposes three standard mixtures of calcium chromate, red lead and lamp black were made which closely matched the tints of both compounds at three stages of darkening. Plates coated with these mixtures were mounted side by side with similar plates coated with the substance under observation, no medium being used, and placed inside a small electrically heated oven with a glass

front. For the direct reaction the plates were illuminated with a 500 c.p. pointolite lamp, and for reversal the oven was kept in the dark and observations made from time to time through a red glass.

The accuracy with which the time of exact matching of the tints could be judged was not very great and consequently a number of readings were taken in each case. The mean values for the times of reversal are shown in Table IV.

TABLE IV
Times for Reversal at Different Temperatures

| Substance | Tints | Time required mins. | | | $t_{40} + t_{60}$ | $t_{50} + t_{60}$ |
|-----------|--------|---------------------|-----|-----|-------------------|-------------------|
| | | 40° | 50° | 60° | | |
| HS.Hg.CNS | 3 to 2 | 61 | 35 | 18 | 1.75 | 1.95 |
| | 2 to 1 | 70 | 39 | 21 | 1.8 | 1.85 |
| I.Hg.CNS | 3 to 2 | 42 | 22 | 12 | 1.9 | 1.85 |
| | 2 to 1 | 48 | 25 | 13 | 1.9 | 1.9 |

As the change in tint from one standard to another corresponds with the transition of a definite proportion of the substance from the dark to the light variety, the times taken to change from one colour to another when the shades do not differ very widely may be taken as approximately inversely proportional to the reaction velocity. Hence the figures in the last two columns represent the temperature coefficients for a change of 10°. It will be observed that they approximate to 1.9 which is a usual figure for a chemical reaction of the ordinary type.

The reaction in light is complicated by the fact that at the higher temperatures the rate of the reverse action is of the same order. It is shown in the next section that the time of darkening is inversely proportional to the intensity of the incident light and hence it is probable that the amount of darkening is proportional to the time of exposure for a limited range. The same does not necessarily hold for the reaction in the dark but it may be assumed to be approximately correct for a small change of colour. Hence if t_1 is the time for a given colour change in the light and t_2 in the dark, the amounts changed in unit time are proportional to $1/t_1$ and $1/t_2$ and when both reactions take place simultaneously the change is proportional to $1/t_1 - 1/t_2$; so that if t is the observed time, $1/t = 1/t_1 - 1/t_2$ giving t_1 in terms of t and t_2 . t_2 is known from the results in Table IV so that t_1 can be calculated. Table V gives the results of the observations.

TABLE V
Times for Darkening at Different Temperatures

| Substance | Tints | t obs. mins. | | | t_1 mins. | | |
|-----------|--------|----------------|------|------|-------------|-----|-----|
| | | 40° | 50° | 60° | 40° | 50° | 60° |
| HS.Hg.CNS | 1 to 2 | 5.3 | 5.6 | 6.2 | 4.9 | 4.9 | 4.8 |
| | 2 to 3 | 5.1 | 5.4 | 6.0 | 4.7 | 4.7 | 4.5 |
| I.Hg.CNS | 1 to 2 | 10.1 | 11.3 | 13.0 | 8.3 | 7.8 | 6.5 |
| | 2 to 3 | 9.7 | 10.9 | 12.1 | 7.8 | 7.3 | 6.0 |

From these it appears that the velocity of transformation of the compound HS.Hg.CNS is unaffected by temperature while for I.Hg.CNS the temperature coefficient is of the order 1.05 from 40° to 50° and 1.2 from 50° to 60°. In the latter case the correction for the reverse reaction is very large, particularly at the higher temperature and it is probable that the simple formula used to obtain t_1 is incorrect. It seems likely therefore that the temperature coefficient for both the substances is in the neighborhood of 1, the characteristic value for a purely photochemical reaction. These results correspond with those of Padoa and Tabellini¹ who, in studying the phototropic transformation of piperil-*o*-tolyl osazone have shown that the temperature coefficient of the direct photochemical reaction is 1.06 while in the dark the corresponding figure is 2.

The Relation Between Light Flux and Phototropic Change

If the quantity of a substance which undergoes phototropic change is proportional only to the total amount of light energy falling upon it, the time of exposure necessary to produce a constant change should be inversely proportional to the light intensity. This has been found to be the case for the substances HS.Hg.CNS and I.Hg.CNS. Measurements were made by coat-

TABLE VI
Relation between Time of Exposure and Light Intensity

| t mins. | Tint 1 | | t | Tint 2 | | t | Tint 3 | |
|-----------|--------|-----|-----|--------|-----|-----|--------|------|
| | I | I.t | | I | I.t | | I | I.t |
| HS.Hg.CNS | | | | | | | | |
| 2 | 100 | 200 | 6 | 67 | 402 | 8 | 100 | 800 |
| 4 | 51 | 204 | 8 | 50 | 400 | 10 | 80 | 800 |
| 6 | 33.5 | 210 | 10 | 40 | 400 | 12 | 67 | 804 |
| 8 | 25 | 200 | 12 | 33.5 | 402 | 14 | 57 | 798 |
| 10 | 20 | 200 | 14 | 29 | 406 | 16 | 50 | 800 |
| 12 | 16.5 | 198 | 16 | 25 | 400 | 20 | 40 | 800 |
| 14 | 14.5 | 203 | 20 | 20 | 400 | 25 | 32 | 800 |
| 20 | 10 | 200 | 30 | 13.5 | 405 | 30 | 27 | 810 |
| 30 | 7 | 210 | 60 | 7 | 420 | 45 | 18 | 810 |
| 60 | 3.5 | 210 | | | | 60 | 13.5 | 810 |
| I.Hg.CNS | | | | | | | | |
| 4 | 100 | 400 | 8 | 100 | 800 | 20 | 100 | 2000 |
| 6 | 67.5 | 405 | 10 | 82 | 820 | 25 | 81 | 2025 |
| 8 | 50 | 400 | 12 | 67.5 | 810 | 30 | 67 | 2010 |
| 10 | 40 | 400 | 16 | 50 | 800 | 35 | 58 | 2030 |
| 12 | 34.5 | 414 | 20 | 40 | 800 | 40 | 50 | 2000 |
| 15 | 26.5 | 398 | 30 | 27 | 810 | 45 | 45 | 2025 |
| 30 | 13.5 | 405 | 60 | 13.5 | 810 | 60 | 33.5 | 2010 |
| 60 | 7 | 420 | 120 | 6.5 | 780 | 120 | 17 | 2040 |

¹Gazz., 45I, 10, (1915).

ing glass plates with the compounds using a very dilute gelatine solution (0.01 per cent.) as binder. The plates were heated for 2 hours at 60° in the dark in order to reverse small quantities of the substance which might have been darkened by accidental exposure to light during preparation and then exposed through a calibrated neutral tint wedge to the light from a 500 c.p. pointolite lamp. Exposures of varying duration were given at a constant distance from the source of light and a strip of graduated intensity thus obtained for each exposure. The portion of this strip which just matched a standard tint was noted and the intensity of the transmitted light at that point ascertained from the calibration of the wedge. Table VI shows the times of exposure and the intensity of the light required to produce a colouration matching each of three different standard tints (the same as those used in the experiments upon the temperature coefficients).

The product I.t is in all cases constant and there is no indication of any period of induction.

Summary

1. Twenty mercury compounds of the types $X.Hg.CNY$ and $Hg.X_2$, $2HgY$ where X is Cl, Br, I, HS, HSe, CNS or CNSe and Y is O, S or Se have been prepared and found to be phototropic.

2. By spectroscopic examination of 10 of the more sensitive of these compounds it has been found that with one exception they are all darkened by exposure to light of wave length of the order of 5500 A.U. and less, slight sensitiveness extending into the ultra-violet to the limit of transmission of quartz. A broad but well defined maximum of sensitiveness is found, usually in the green. The position of the maximum for related compounds tends to move towards the red with increase in molecular weight.

3. If the compounds are previously darkened by exposure to light, reversal can be effected by exposing to red light in the spectroscope. No maximum could be detected, but there was a limiting wave length on the short wave side beyond which no reversal occurred. In several cases this point was too far in the red to be determined. Between the reversal region and the region sensitive to light was a neutral zone in which no action took place. Reversal was in all cases brought about by heat.

4. The effect of various media has been examined. In most cases the direct reaction is accelerated by a medium such as gelatin, but the reverse reaction is always retarded.

5. The region sensitive to light can be extended towards the red by dyeing the compounds as in the case of the photographic plate.

6. The temperature coefficients of the direct (light) and reverse (dark) reactions have been measured for two compounds and found to be approximately 1.0 and 1.9 respectively.

7. The time of exposure necessary to produce a given change has been found inversely proportional to the intensity of the light. No induction period has been observed.

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February 27, 1928.*

STUDIES ON GLASS

II. The Transition between the Glassy and Liquid States in the Case of Glucose

BY GEORGE S. PARKS, HUGH M. HUFFMAN AND FRANCIS R. CATTOIR

In the first paper¹ of this series we frankly abandoned the widely prevalent idea that a glass is simply an undercooled liquid which, upon being heated, changes gradually and regularly in its properties to produce the stable liquid state. By our studies upon the transition of certain organic glasses, especially those of n-propyl alcohol, propylene glycol and glycerol, we were led to a somewhat different conclusion. "While there is no definite temperature, comparable to the melting point of a crystal, at which all properties undergo a sharp change, there is nevertheless a temperature interval, definite and reproducible, in which a number of properties change with a rapidity approaching that observed in the case of the melting process of a crystal. In brief, there is a softening region instead of a melting point. The glass as it exists below this softening region differs so markedly from the liquid existing above that it might well be considered as a different state of the substance." For this reason we suggested the possibility of regarding glass as a fourth state of matter, distinct from both the liquid and crystalline states and yet showing to some extent characteristics of both these states. A promising alternative hypothesis involved the view that it is a colloid very much analogous to a jelly. According to this last explanation the softening region represents the temperature range through which the jelly changes into an associated liquid.

In this earlier paper we made no attempt to choose between these two hypotheses or, indeed, to exclude other possibilities, since we possessed experimental data for only two or three properties, such as the specific heat and the coefficient of thermal expansion. Moreover, any more extensive investigation of the transition in these glasses, naturally including the study of other physical-chemical properties, would have encountered very serious difficulties, owing to the low temperatures involved. Accordingly, we have carried on a search for a simple, stable organic glass which might show a transition in a region of the temperature scale more suitable for extensive experimental work. After a considerable number of tests we have finally selected d-glucose (dextrose) for our study. This substance can be converted into a pure, fairly stable glass, which then exhibits properties exactly similar to those shown by the alcohol glasses previously studied and furthermore undergoes the transition to the liquid condition in the neighborhood of room temperature. Using this material, we are now engaged in an extensive investigation of the glassy state of matter and of its transition to the liquid state.

¹ Parks and Huffman: *J. Phys. Chem.*, **31**, 1842 (1927).

The present paper contains a description of the glucose glass, together with our experimental data for its specific heat, coefficient of thermal expansion and refractive index.

The Glucose Glass

In the preliminary preparation of glassy specimens, samples of C. P. crystalline d-glucose from several sources were employed. However, the material prepared by the Special Chemicals Company proved to be the best of these and consequently was used as the starting point in the preparation of glasses for all our quantitative work. This "Pfanstiehl" anhydrous glucose was a white, finely crystalline product. According to the manufacturer's description, it had a specific rotation of 52.5° and contained 0.10% of water but was free from dextrin, maltose or inorganic impurities. Two combustion analyses, made upon it by Dr. Hashimoto of this laboratory, gave respectively: hydrogen, 6.60% and 6.64%; carbon, 40.03% and 40.11%. The results agree within the limits of analytical error with the calculated values for pure anhydrous glucose: hydrogen, 6.71% and carbon, 39.98%.

The crystalline glucose melts at 146°C . and the product, upon being heated up to 160° for ten or fifteen minutes, can be converted into a clear, mobile liquid. When this liquid is cooled, it increases rapidly in viscosity and finally sets to a hard glass in the neighborhood of 40°C . In our earlier preparations the glass was usually straw-colored or light brown, owing to a slight initial color in the crystals and to a small amount of decomposition at the higher temperatures; furthermore, it contained numerous minute bubbles which marred its optical clearness. We therefore purified our crystalline glucose by the method of Hudson and Dale¹ before starting the preparation of the glasses. Then, by use of a vacuum over the liquid at 160° , the larger bubbles could be eliminated within a much shorter period of heating, while the application of 4 atm. pressure of nitrogen gas upon the liquid glucose during the cooling process served to cause the disappearance of the smaller bubbles. With this procedure some excellent samples of clear, colorless glass were prepared.

When liquid glucose is heated above 174°C . for a considerable period of time, Beilstein² states that water is lost out of the glucose molecule and glucosan ($\text{C}_6\text{H}_{10}\text{O}_6$) results. As in many of our preliminary experiments we noticed the evolution of a small amount of water which condensed in the cold parts of our apparatus, it seemed desirable to check up carefully on the possibility of this chemical change taking place during the preparation of our glass samples. Accordingly, after preparing a distinctly brown specimen of the glass, we reheated it under vacuum at 170° for about half an hour and then chilled the product. The conditions of temperature and time of heating under a vacuum in this particular experiment were thus far more favorable toward deterioration of the glucose than in any actual preparation of one of our working samples. The resulting material was dark brown in color and

¹ Hudson and Dale: *J. Am. Chem. Soc.*, 39, 324 (1917).

² Beilstein's "Handbuch der organischen Chemie," 882 (1918).

inferior in appearance to the glasses employed in our quantitative measurements. However, three combustion analyses gave the following results: carbon, 40.28%, 40.37% and 40.45%; hydrogen, 6.65%, 6.63% and 6.60%. As glucosan contains 44.42% carbon, it is evident that here we have less than 9% conversion of glucose into glucosan. Samples of the glasses employed in our specific heat and expansion measurements were also analyzed and found to have a carbon and hydrogen content practically identical, within the limits of analytical error, with that of pure glucose. These glasses will be described further in connection with the particular measurements involved; but the point which we wish to make at the present time is that we are here dealing with relatively pure glucose glass rather than with possible anhydride products.

Glucose glass is a fairly stable or, more properly speaking, rather inert material and at room temperature can be kept in dry air or under xylene for months without showing any signs of crystallization. However, every pure sample that we have ever made has crystallized eventually and when the process once starts it proceeds slowly but surely to completion. An interesting point in this connection is that crystallization appears to start always at an interface rather than within the solid glass. For this reason glass samples which contain numerous bubbles crystallize more readily than specimens which are without such flaws. Traces of water, or of any other liquid in which the glucose is somewhat soluble, also promote the devitrification process.

We have carried out a few preliminary experiments to test the relative solubility of glassy and crystalline glucose in 99% ethyl alcohol and in absolute ethyl alcohol, isopropyl alcohol and acetone. Some of the results obtained at about 23°C. are shown in Table I. While as yet this phase of the investigation has not been brought to completion, the ratios of the solubilities (Column 4) show clearly the thermodynamic instability of the glass with reference to the crystallization process.

TABLE I
Solubilities of Glassy and Crystalline Glucose at 23°C.
(In grams of glucose per 100 grams of solvent)

| Solvent | Glass | Crystals | Ratio: Glass/Crystals |
|------------------------|-------|----------|-----------------------|
| 99% Ethyl Alcohol | 4.70 | 0.44 | 10.7 |
| Pure Ethyl Alcohol | 1.58 | 0.22 | 7.2 |
| Pure Isopropyl Alcohol | 1.07 | 0.08 | 13.4 |
| Pure Acetone | 0.184 | 0.014 | 13.2 |

This simple glucose glass which we have been describing can be used as the basis for the preparation of more complicated organic glasses, just as silica when mixed with other inorganic materials produces the various commercial glasses. Thus for instance, the addition of 10% of water to the pure glassy glucose produces a two component glass with apparently similar properties except that the softening point is lowered about 50°. Another interesting glass can be made by dissolving sodium acetate to the extent of about 1% in the liquid glucose. This product in the glassy state is a very

poor conductor of the electric current, but above its softening point the conductivity increases rapidly. Thus, we have found the conductance of a sample at 75° to be about ten times and at 90° about one hundred times the conductance at 60° . This phenomenon is apparently similar to that observed in connection with the electrical conductivity of ordinary soda-lime glass.¹

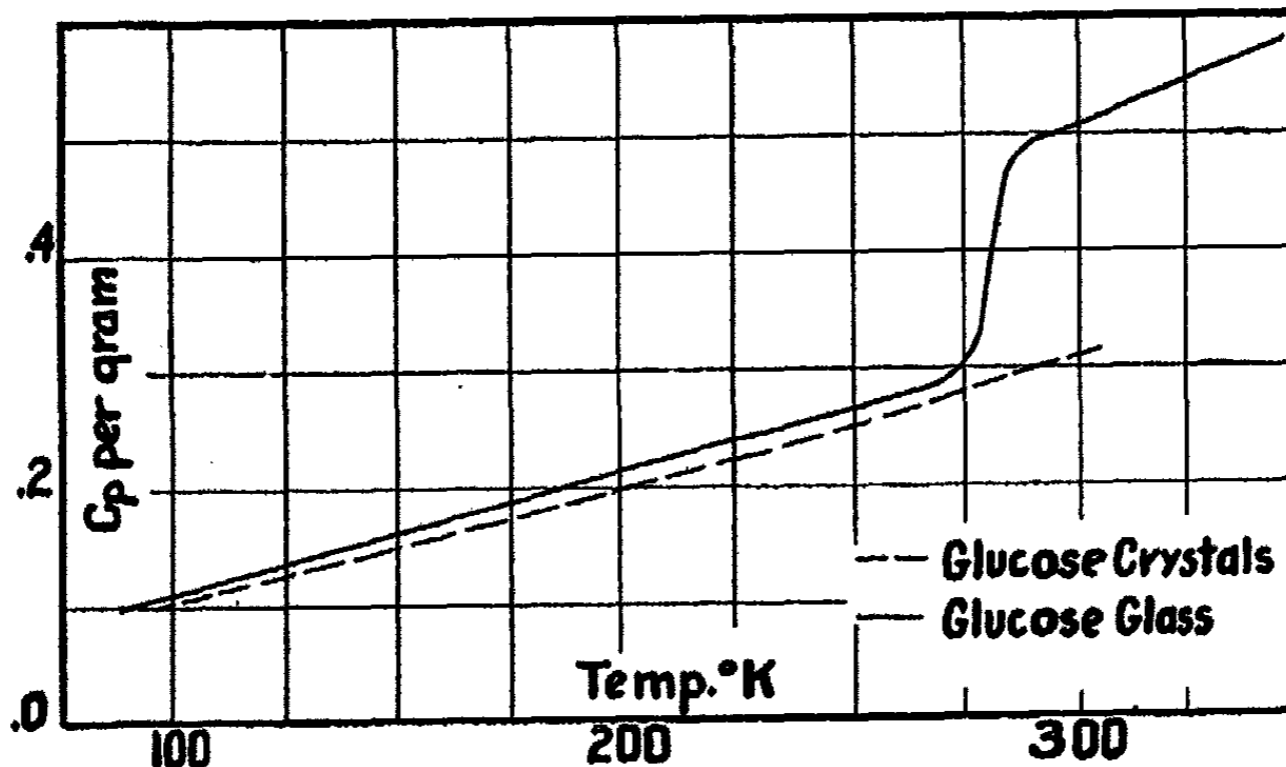


FIG. 1

Heat Capacity Data

The heat capacities of glassy and liquid glucose were determined over the temperature range from 90° to 343°K (i.e. to 70°C). In principle, the method of Nernst was employed with an aneroid calorimeter in obtaining the "true" or instantaneous specific heats. A measured amount of heat was supplied by an electric current to the substance contained in a copper calorimeter, which was suspended in a vacuum and surrounded by a silvered copper cylinder in order to diminish the conduction and radiation of heat to and from the surroundings. A thermocouple in the center of the calorimeter measured the rise in temperature. The entire apparatus and details of experimental procedure have been fully described previously.²

The specific heat results appear in Table II and are represented graphically in Fig. 1. Considering possible systematic and fortuitous errors together, we estimate these values to be accurate to within 2.0%. Moreover, the fortuitous errors in any particular determination produce no deviations from the curve in excess of 0.6%, a fact which indicates the reliability of the data for comparative purposes. The heat capacity-temperature curve in

¹ See for example Kraus: "The Properties of Electrically Conducting Systems," 357 (1922).

² Parks and Kelley: *J. Phys. Chem.*, 30, 47 (1926).

this case¹ is essentially similar to those observed for the alcohol glasses previously studied. Thus, up to 275°K. the specific heat curve for glucose glass is but slightly higher than the corresponding one obtained by Simon² for crystalline glucose, but above this point there is a sharp 62% increase in heat capacity within an interval of 12° and the curve becomes continuous with that for the liquid state. The material, however, is not noticeably soft below 310° and only becomes sufficiently liquid to permit of the ready turning of a stirring rod within it at about 330°K.

The slightly yellow sample of glucose glass employed in these measurements was allowed to remain in the sealed calorimeter for over six months following the completion of the work. It was then removed and found to be entirely crystalline—an important indication of its purity. A portion of it was subsequently analyzed with the following results: 1st. analysis, 6.76% hydrogen and 39.80% carbon; 2nd. analysis, 6.86% hydrogen and 39.80% carbon. These data are in good agreement with the theoretical values for pure glucose.

TABLE II
Specific Heats of Glucose Glass and Liquid
(In terms of the 15° calorie)

| Temp., °K. | C _p per gram | Temp., °K. | C _p per gram |
|------------|-------------------------|------------|-------------------------|
| 94.1 | 0.1045 | 280.3 | 0.3541 |
| 102.9 | 0.1135 | 281.1 | 0.3744 |
| 109.0 | 0.1201 | 282.7 | 0.4035 |
| 126.1 | 0.1373 | 284.0 | 0.4329 |
| 150.5 | 0.1613 | 285.8 | 0.4634 |
| 174.7 | 0.1857 | 285.8 | 0.4694 |
| 188.1 | 0.1990 | 287.1 | 0.4803 |
| 193.5 | 0.2052 | 289.0 | 0.4865 |
| 198.5 | 0.2121 | 289.3 | 0.4889 |
| 202.6 | 0.2147 | 290.5 | 0.4906 |
| 207.5 | 0.2209 | 292.8 | 0.4946 |
| 224.4 | 0.2408 | 294.0 | 0.4990 |
| 243.3 | 0.2596 | 294.8 | 0.5011 |
| 253.4 | 0.2684 | 300.1 | 0.5099 |
| 263.8 | 0.2811 | 300.5 | 0.5066 |
| 274.7 | 0.3017 | 307.7 | 0.5178 |
| 275.1 | 0.3013 | 315.9 | 0.5294 |
| 275.9 | 0.3077 | 323.9 | 0.5468 |
| 276.1 | 0.3076 | 332.8 | 0.5573 |
| 278.0 | 0.3197 | 339.8 | 0.5673 |
| 279.3 | 0.3311 | | |

¹ Following the completion of our experimental work, a very interesting paper was published by Tammann and Tampke: *Z. anorg. allgem. Chem.*, 162, 1 (1927). For the change in heat capacity of glucose glass over the temperature range 260° to 310° K., these investigators obtained a rough qualitative curve which is in essential agreement with the quantitative data presented here.

² Simon: *Ann. Physik*, 68, 258 (1922).

The experimental results are for C_p , the specific heat at constant pressure. However, C_v , the specific heat at constant volume, can be obtained indirectly by the well-known equation

$$C_v = C_p - \frac{0.0242 \alpha^2 VT}{\beta}$$

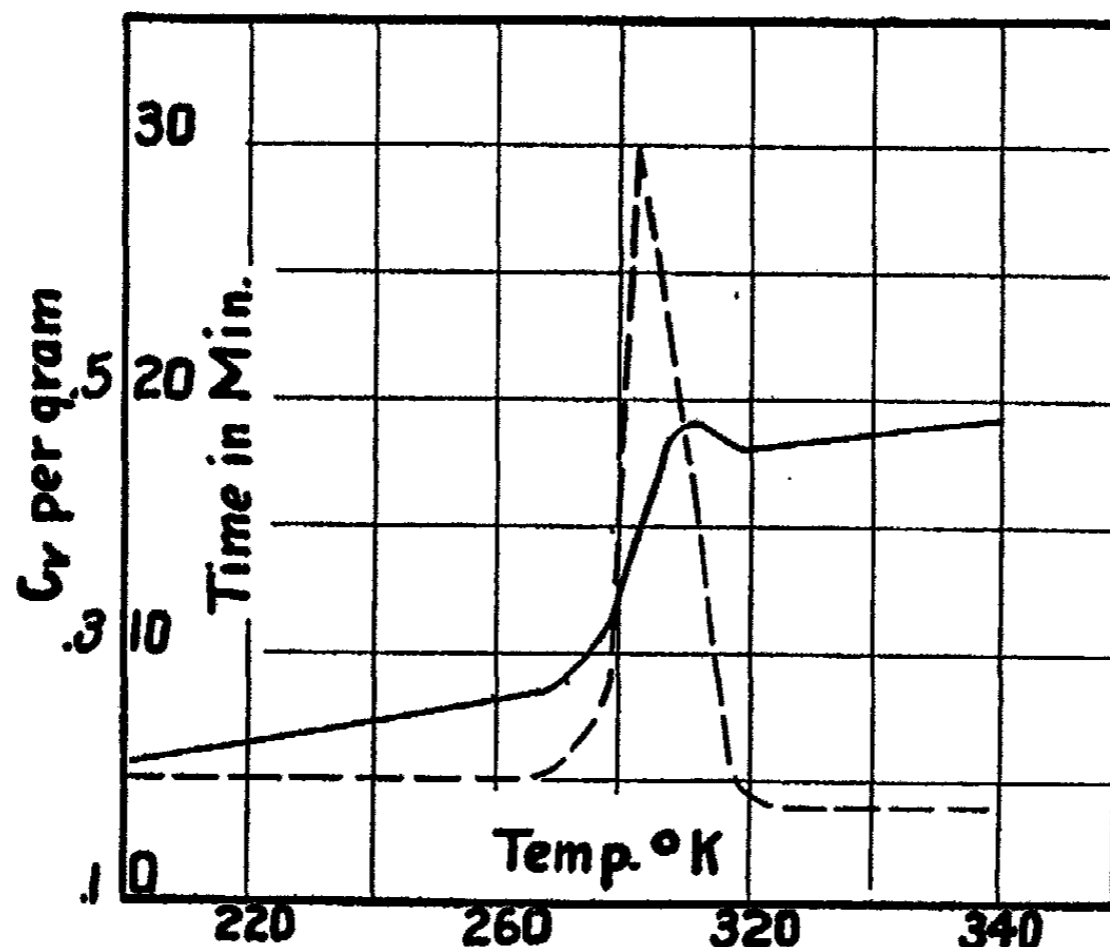


FIG. 2

The solid line represents C_v plotted against temperature. The broken line represents the time for thermal equilibrium in the specific heat runs plotted against the temperature.

where α is the coefficient of thermal expansion and β is the coefficient of compressibility of the substance. From a theoretical standpoint C_v has often proved to be of greater interest than C_p . Hence, in the present case we have calculated the values of C_v at a number of temperatures. For the coefficient of thermal expansion in this calculation we have used the data which will be described in the following section of this paper, while for the coefficient of compressibility we have employed $13(10^{-6})$ over the entire temperature range. This particular value was selected after a careful study of the data obtained by Cowper and Tammann¹ for glucose in the crystalline and glassy states. The results for C_v appear in Table III and are represented graphically in Fig. 2. It is interesting that the curve for C_v shows a decided maximum in the temperature region around 290°K (17°C.), which falls in rather closely with the maximum obtained by plotting the times required for attaining thermal equilibrium in the specific heat runs against the corresponding tem-

¹ Cowper and Tammann: *Z. physik. Chem.*, 68, 286 (1909).

peratures. Both curves thus indicate the existence of a transition region involving the absorption of heat and, in order to bring out this point more clearly, we have plotted them in the same figure.

TABLE III
Specific Heats of Glucose Glass and Liquid
(In terms of the 15° Calorie)

| Temp., °K. | C _v per gram | Temp., °K. | C _v per gram |
|------------|-------------------------|------------|-------------------------|
| 200.0 | 0.211 | 295.0 | 0.472 |
| 265.0 | 0.279 | 298.0 | 0.460 |
| 275.0 | 0.298 | 300.0 | 0.463 |
| 280.0 | 0.342 | 305.0 | 0.469 |
| 288.0 | 0.479 | 320.0 | 0.486 |
| 290.0 | 0.484 | 340.0 | 0.512 |

Expansion Data

In the previous study we believed that we had evidence of a marked increase in the coefficient of thermal expansion of propylene glycol at a temperature *just above* the region in which the sudden rise in heat capacity takes place. However, the method employed was by no means free from criticism and therefore one of our first aims in the present investigation has been to obtain accurate data for the coefficient of thermal expansion of glucose glass.

Two methods have been used in this work. The first consisted simply in determining the densities of the glucose glass by weighing samples immersed in toluene in a calibrated specific gravity bottle. About sixty determinations were made over a temperature range between 275° and 330°K. The results were not satisfactory for evaluating the coefficient of expansion, altho in general they indicated that there was a rather sharp increase at about 300°. Above this point the coefficient was apparently about double the value below it. The density of the glucose glass according to these measurements was 1.523 at 20°C.

The second method employed a dilatometer and, as finally developed, gave much more reliable values for the coefficient of thermal expansion. In our earlier work this dilatometer consisted of a 50 cc spherical, Pyrex bulb, from the top of which projected vertically a long tube of semi-capillary bore. Small sticks of glucose glass were introduced into the bulb thru a short entry tube in its side, which was then sealed off quickly with a minute flame. The free space in the dilatometer was next filled with pure, dry xylene thru the open end of the semi-capillary tube. After evacuation of the air in the vessel, this tube was sealed at its top. The dilatometer bulb was then placed in a 3-liter Dewar jar which served as a small, adjustable thermostat. The jar was filled with water and, equipped with a stirrer, thermometer and electrical heating coil, could be adjusted to practically any desired temperature. By measuring the rise of the xylene in the vertical tube as progressively higher temperatures were attained and subtracting the part of this rise due to the expansion of the xylene itself, the coefficient of thermal expansion of the

glucose glass could be obtained for each temperature increment. The results showed a sharp two or threefold increase in the coefficient of the glass between 293° and 303°K. Two sets of runs with different Pyrex dilatometers checked qualitatively but the actual numerical values were rather uncertain, owing to the fact that the volumes of the glucose and the xylene in these dilatometers were about equal, while the expansion coefficient for the latter was several times that of the glucose.

We next devised a metal dilatometer which proved much more satisfactory. This consisted essentially of a cylindrical brass can with walls about 3 mm. thick. The can was fitted with a brass top which screwed into place and could be made vacuum-tight by means of a small lead gasket. A brass connecting tube, 25 cm. long and about 4 mm. in diameter, ran vertically from this top to a uniform glass tube, 1 mm. in internal diameter and about 150 cm. long. The connecting tube was brazed into the metal top of the can and was cemented to the glass dilatometer tube by means of shellac. This metal dilatometer, when set up, had a capacity of about 51 cc and could carry a solid, cylindrical sample of glucose glass of 40 to 45 cc in volume. The small remaining space between the glucose sample and the walls of the container was filled with pure, dry xylene which had been previously freed from air by boiling under a vacuum. The amount of xylene was adjusted so as to give a convenient height of liquid in the glass dilatometer tube at room temperature. The upper end of this tube was then closed by a loosely-fitting glass plug, which practically eliminated any evaporation loss of xylene while at all times insuring the existence of barometric pressure within the apparatus. As before, the Dewar jar was utilized as a small, adjustable thermostat and all the measurements were carried out in a constant temperature room so as to eliminate the effect of temperature changes on the liquid in the glass dilatometer tube.

Two different series¹ of data, obtained with this apparatus, are given in Tables IV and V, respectively. In Column 2 are the observed heights of xylene in the dilatometer tube corresponding to the various thermostat temperatures of the first column. These observed heights were measured from a purely arbitrary zero point and their differences were then used in obtaining the values for $\Delta h/\Delta T$, which appear in the next column of each table. The values for $\Delta h/\Delta T$ represent the resultant effect due to the expansion of the xylene used as a dilatometric fluid, the expansion of the glucose and the expansion of the brass dilatometer with increasing temperatures. The fourth column contains the net rise due to the glucose in millimeters of the dilatometer tube per degree, allowance having been made for the expansion of the xylene and the brass dilatometer. The last column then contains the coefficients of cubical expansion of the glassy and liquid glucose calcu-

¹ In each case the measurements were carried out in the order of increasing temperatures but different samples of glassy glucose were employed in the two series. A pair of analyses made upon similar material gave the following results: carbon, 40.08% and 39.98%; hydrogen, 6.66% and 6.63%, respectively. Thus, the glasses had a composition corresponding to pure $C_6H_{12}O_6$.

lated therefrom. For these calculations the volume of the dilatometer tube per millimeter was measured by two series of calibrations, one with pure water and the other with mercury, and found to be 0.00118 cc per mm. The expansion of the xylene alone was determined in an independent series of measurements with the dilatometer entirely filled with this liquid. After allowing for the expansion of the brass cylinder with temperature, we obtained $\Delta h/\Delta T = 43.5$ mm/deg. for the 50.7 cc of xylene involved. From this value we calculate the cubical expansion for liquid xylene to be $10.1(10^{-4})$. The use of xylene and toluene as dilatometer liquids was justifiable, because they have no chemical effect on glucose and do not dissolve this material in either the glassy or crystalline forms to any measurable extent.

Using this method, we also measured the coefficient of cubical expansion of crystalline glucose over the temperature range $273^{\circ} - 323^{\circ}\text{K.}$ and found it to be uniform and equal to $0.84(10^{-4})$.

TABLE IV
Dilatometer Data on Glucose Glass and Liquid, Series I.
(Weight of glucose glass, 64.46 gm.; weight of xylene, 7.40 gm.)

| Temp., °K. | Capillary height, h | $\Delta h/\Delta T$ | Net rise for glucose, $\Delta h'/\Delta T$ | Coefficient $1/V (dV/dT)$ |
|------------|---------------------|---------------------|--------------------------------------------|---------------------------|
| 273.11 | 0.0 mm. | | | |
| | | 8.82 | 3.91 | 1.09 (10^{-4}) |
| 278.86 | 50.7 " | | | |
| | | 9.25 | 4.34 | 1.21 " |
| 283.76 | 96.0 " | | | |
| | | 9.01 | 4.10 | 1.14 " |
| 293.38 | 182.7 | | | |
| | | 14.90 | 9.99 | 2.76 |
| 298.24 | 255.2 | | | |
| | | 16.55 | 11.64 | 3.25 |
| 303.18 | 377.0 | | | |
| | | 17.20 | 12.29 | 3.43 |
| 308.76 | 433.0 | | | |
| | | 17.20 | 12.29 | 3.43 |
| 313.30 | 510.0 | | | |
| | | 18.05 | 13.14 | 3.67 |
| 320.46 | 640.3 | | | |
| | | 18.30 | 13.39 | 3.73 |
| 333.46 | 878.2 | | | |
| | | 18.40 | 13.49 | 3.76 |
| 348.61 | 1,157.0 | | | |

In each series of measurements upon glassy glucose, the values for the expansion coefficient show a sharp increase of approximately 200% within the temperature interval $293^{\circ} - 303^{\circ}\text{K.}$ (Fig. 3). Below this transition region, the coefficient for the glass is somewhat larger than that for the crystalline form but certainly of the same order of magnitude. Above this

TABLE V
Dilatometer Data on Glucose Glass and Liquid, Series 2.
(Weight of glucose glass, 66.54 gm.; weight of xylene, 6.49 gm.)

| Temp., °K. | Capillary height, h | $\Delta h/\Delta T$ | Net rise for glucose, $\Delta h'/\Delta T$ | Coefficient $1/V (dV/dT)$ |
|------------|---------------------|---------------------|--------------------------------------------|---------------------------|
| 262.50 | -81.0 mm. | | | |
| | | 7.64 | 3.63 | 0.98 (10^{-4}) |
| 273.11 | 0.0 " | | | |
| | | 7.99 | 3.98 | 1.08 " |
| 282.94 | +78.5 " | | | |
| | | 8.61 | 4.60 | 1.24 " |
| 293.54 | 169.7 | | | |
| | | 14.34 | 10.33 | 2.79 |
| 296.26 | 208.7 | | | |
| | | 18.52 | 14.51 | 3.92 |
| 299.91 | 276.3 | | | |
| | | 17.45 | 13.44 | 3.63 |
| 302.76 | 326.0 | | | |
| | | 17.15 | 13.14 | 3.55 |
| 305.85 | 379.0 | | | |
| | | 17.18 | 13.17 | 3.56 |
| 308.18 | 419.0 | | | |
| | | 17.24 | 13.23 | 3.57 |
| 314.00 | 519.3 | | | |
| | | 17.86 | 13.85 | 3.74 |
| 322.55 | 672.0 | | | |
| | | 17.25 | 13.24 | 3.58 |
| 328.45 | 773.7 | | | |
| | | 17.43 | 13.42 | 3.62 |
| 344.50 | 1,053.5 | | | |

region the coefficient of the rapidly softening glass is identical with that of the liquid and amounts to about four times that of the crystals. Thus the change in coefficient in going from the glassy to the liquid state is roughly equal to that in going from the crystalline to the liquid state. However, this change in expansion coefficient in the glass-to-liquid transformation takes place in a temperature interval of about 10° and not at a definite point on the temperature scale as in the crystal-to-liquid transformation. Moreover, it should be noted that the change in expansion rate comes at a temperature about 15° above the corresponding sharp change in heat capacity described in the preceding section. This last feature seems rather surprising at first glance but apparently holds true for all the glasses thus far studied.

Before passing, we should note that above this transition region in the expansion coefficient our measurements were very reproducible and the attainment of thermal equilibrium was rapid. In fact, the material behaved

like an extremely viscous liquid. On the other hand, below this region the measurements showed a distinct hysteresis effect with the lapse of time and the attainment of even apparent equilibrium was relatively slow. Accordingly the results for the glass were never strictly reproducible with different samples or with different heat treatments of the same sample. Of course, this is well known to be also the experience with commercial, inorganic glasses and the region of increased expansion rate obtained in heating up a glass is very properly termed "the annealing range."

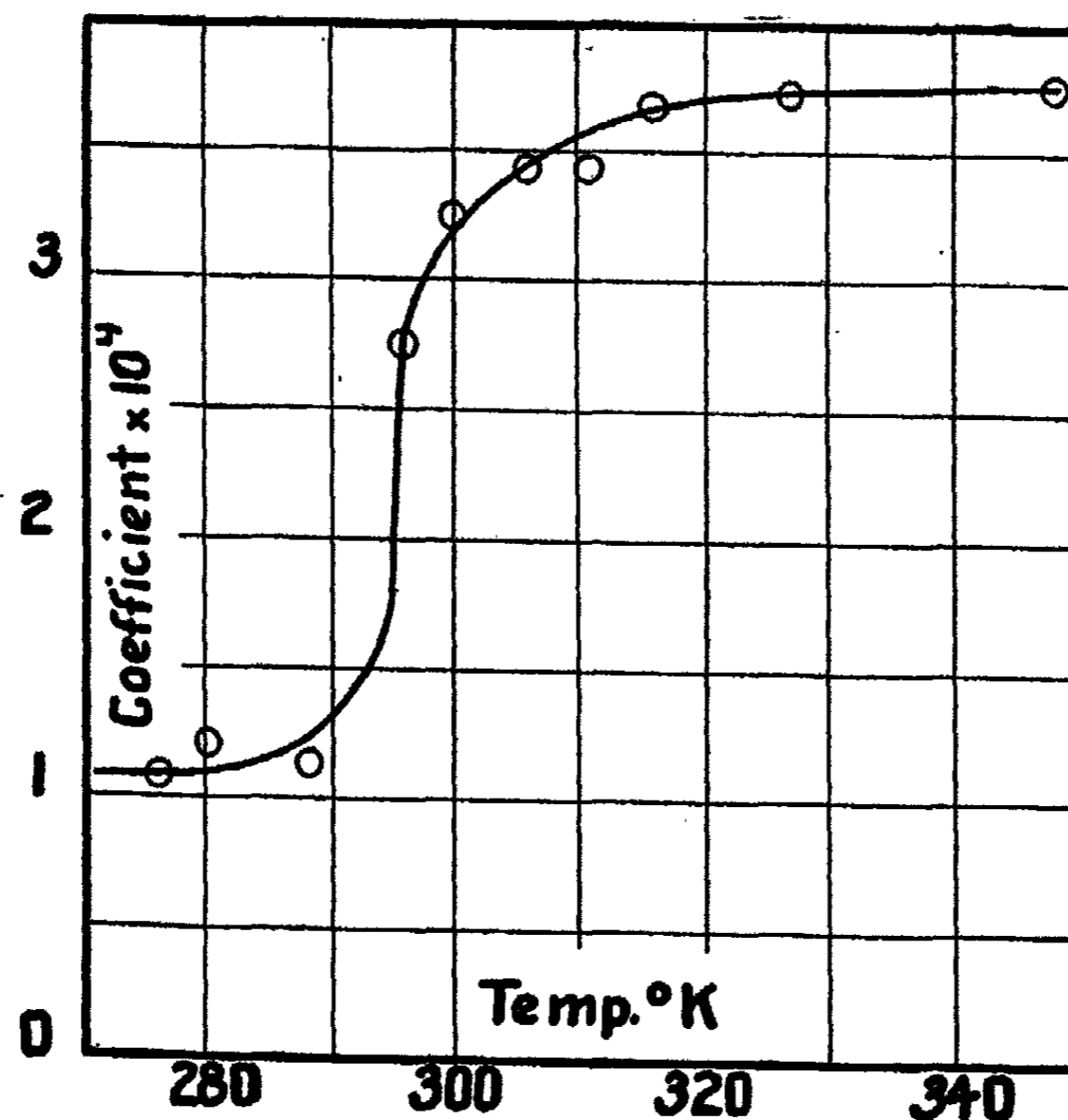


FIG. 3
The expansion coefficients of Series I plotted against the corresponding temperatures.

Refractive Indices

As a further test of the change in properties with increasing temperature, measurements were made on the refractive index of two samples of glucose glass. The prepared glasses were heated until they changed to viscous liquids, which were then poured into two prism cells of a Zeiss-Pulfrich refractometer. The sample in Prism Ic was colorless but apparently contained small dust particles. These were probably obtained from the filter paper used during the purification of the original glucose by the method of Hudson and Dale. The sample in Prism IIc had been prepared directly by heating

the C.P. crystalline glucose and was optically clear, altho slightly yellow in color. In succession these prisms were mounted in the refractometer, the metal cap for the regulation of temperature was put in place and a layer of paraffine was poured into the top of the cell to protect the glucose glass from the moisture in the air. During a determination the temperature was controlled by circulating water through the refractometer system from a small, adjustable thermostat. The temperature of the glucose glass was measured by means of a copper-constantan thermocouple, the hot junction being

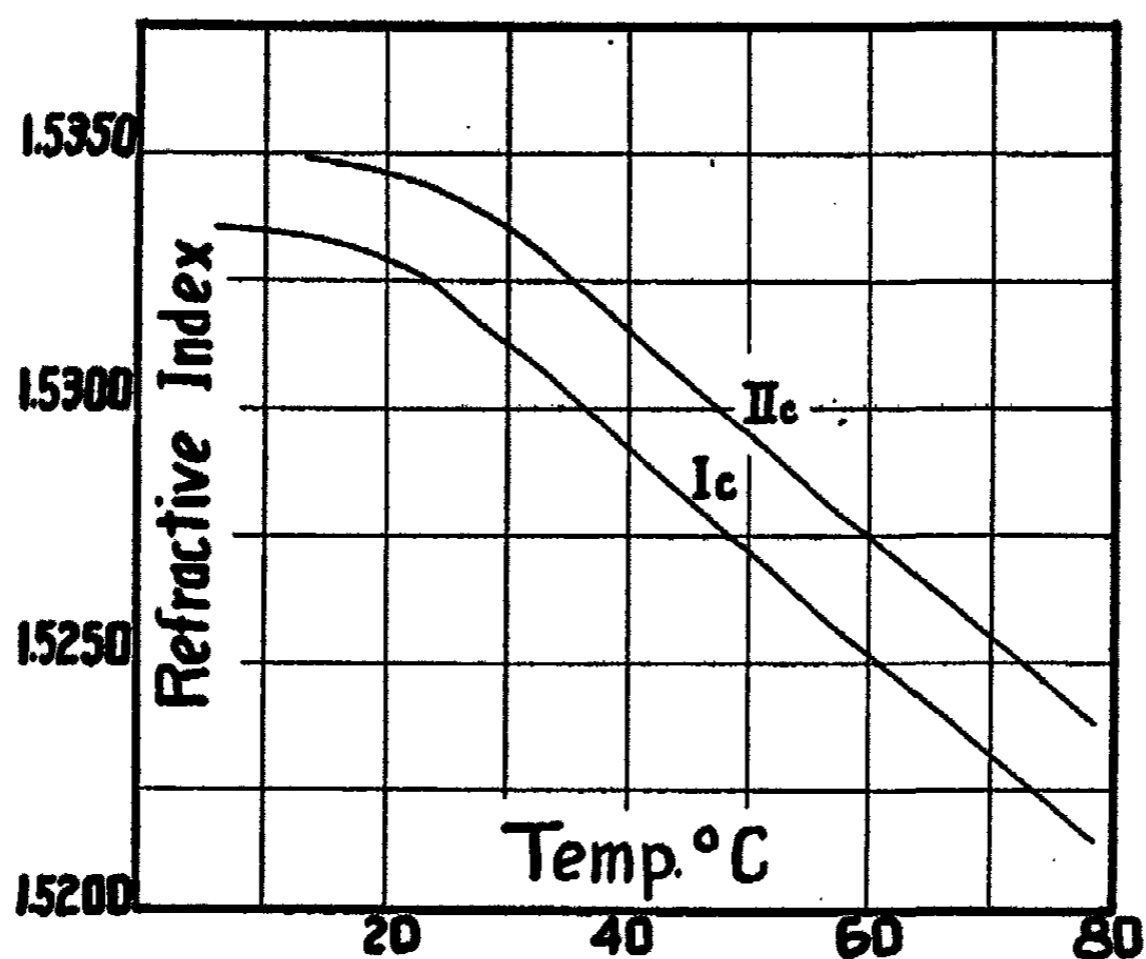


FIG. 4

imbedded therein. Measurements were made with sodium light both during the process of cooling and of heating the samples. It was found impossible to cool the glass in Prism IIc below 16.5°C. without the development of cracks which prevented further readings on the angle of refraction. The results of the measurements are given in Table VI and are shown graphically in Fig. 4.

These two sets of data on different samples of glucose glass differ somewhat but they agree in showing a break between 20° and 30°C. in the rate of change of the refractive index with temperature. Recently Peters,¹ working on a series of commercial, inorganic glasses at the United States Bureau of Standards, has found a similar marked decrease in refractive index within "the annealing region," followed, however, by some indications of an increase as the liquid state was attained. The measurements given here do not show this increase within the range investigated, altho they

¹ Peters: Bur. Standards Sci. Paper, 20, 635 (1926).

TABLE VI
Refractive Indices of Glucose Glass and Liquid

| | Prism Ic Temp., °C. | Refractive index | | Prism IIc Temp., °C. | Refractive index |
|-----------|------------------------|---------------------|-----------|-------------------------|---------------------|
| (Cooling) | 70.9 | 1.5228 | (Cooling) | 50.0 | 1.5294 |
| (") | 67.5 | 1.5234 | (") | 40.8 | 1.5315 |
| (") | 60.6 | 1.5250 | (") | 33.6 | 1.5331 |
| | 55.2 | 1.5263 | | 27.9 | 1.5341 |
| | 43.7 | 1.5285 | | 22.1 | 1.5345 |
| | 25.4 | 1.5322 | | | |
| | 21.0 | 1.5329 | (Heating) | 64.9 | 1.5264 |
| | 18.4 | 1.5329 | (") | 73.4 | 1.5249 |
| | 14.9 | 1.5332 | | | |
| | 11.6 | 1.5334 | (Cooling) | 64.5 | 1.5266 |
| | 10.4 | 1.5335 | (") | 50.6 | 1.5289 |
| | 8.7 | 1.5336 | (") | 41.3 | 1.5314 |
| | 7.0 | 1.5336 | | 31.4 | 1.5333 |
| | | | | 27.0 | 1.5341 |
| (Heating) | 22.1 | 1.5329 | | 22.0 | 1.5346 |
| (") | 28.6 | 1.5315 | | 16.5 | 1.5348 |
| (") | 35.4 | 1.5304 | | | |
| | 39.3 | 1.5292 | | | |
| | 49.9 | 1.5272 | | | |
| | 57.6 | 1.5255 | | | |
| | 67.0 | 1.5236 | | | |
| | 77.1 | 1.5217 | | | |

went well above the temperature at which the glass became a viscous liquid; and, as experimental difficulties made it impractical to carry the investigation to either higher or lower temperatures, it is impossible to say whether the curve obtained with the organic glass would correspond to that for the inorganic or not. Nevertheless, the results do show conclusively that the index of refraction of the glucose glass changes rapidly as the glass-to-liquid transition range is reached. Moreover, it should be noted that the temperature at which the marked decrease starts coincides roughly with that for the change in the coefficient of thermal expansion previously described.

Summary

We may summarize our results as follows:

(1) When crystalline glucose (dextrose) is melted and the resulting liquid cooled down to room temperature, a clear organic glass is obtained. This material softens noticeably at about 40°C. and becomes a thick, viscous liquid at 60°C. Analyses show that it corresponds to the theoretical formula, $C_6H_{12}O_6$.

(2) The specific heat of this material has been measured over the temperature range 90° - 340° K. The results show a sharp 62% increase in the temperature interval 275° - 287° K (i. e. 2° - 14° C.).

(3) The coefficient of thermal expansion has been measured over the temperature range 262° - 348° K. The results show a sharp 200% increase in the interval 293° - 303° K (i.e. 20° - 30° C.).

(4) The refractive index has been measured over the temperature range 7° - 77° C. The index-temperature curve shows a decided change in slope within the interval 20° - 30° C.

At the present time we are continuing the investigation of the properties of glucose glass and for this reason we shall reserve our discussion of the theoretical aspects of the problem for a subsequent paper.

*Department of Chemistry,
Stanford University, California,
March, 1, 1928.*

A MICRO METHOD FOR THE DETERMINATION OF VAPOR PRESSURE AND WATER OF HYDRATION OF SOLID COMPOUNDS*

BY FRANK E. E. GERMANN AND O. B. MUENCH

I. Introduction

In the course of work on platinocyanides now in progress in this laboratory, it became evident that a method was needed for the accurate determination of the vapor pressure and number of molecules of water of crystallization of the various crystalline hydrates. For rapidity of work, as well as for economy of materials in the case of rare or expensive compounds, a method requiring a relatively small amount of sample is to be desired. A knowledge of the vapor pressure of the crystals leads to a method for the preparation and preservation of the hydrates in a pure state, without being contaminated by lower or higher hydrates.

As a result of the very tedious and time-consuming methods used in the past, our knowledge of the various possible hydrates is very meagre. In the case of copper sulphate, various experimenters have established the existence of compounds containing 5, 3, 1 and 0 molecules of water of crystallization. In the case of uranyl nitrate some evidence has been adduced showing the existence of compounds¹ containing 24, 6, 3, 2, 1 and 0 molecules of water, but the actual proof for the 2 and 1 has not been given. In most cases, however, we only know of the existence of the normal hydrate crystallizing from water at room temperature. The lower hydrates are sometimes prepared by crystallizing from acid solutions or solutions of the compound in alcohol containing various amounts of water. These methods, however, involve the possibility of introducing impurities and alcohol of crystallization.

In general, we attach little importance to a knowledge of the lower hydrates, other than the cataloging of all possible compounds, phase rule equilibria, etc. However, in the case of the uranyl salts, very careful measurements were made by Nichols and Merritt² on the fluorescence spectra of the various compounds, as well as on the various hydrates of the same salt. An attempt was made to find some relation between the fluorescence spectra and the number of molecules of water of crystallization. A similar study, undertaken by the former of us, shows that water of crystallization has a very profound influence on the fluorescence spectra of the platinocyanides. A careful examination of the literature revealed that the data on the existing hydrates of the platinocyanides were very conflicting. The usual methods of analysis are not available, since even momentary exposure of the salt hydrate to air frequently causes very profound changes in color, which accompany changes in water of crystallization.

* Contribution from the Department of Chemistry of the University of Colorado.

¹ Germann: *J. Am. Chem. Soc.*, **44**, 1466 (1922).

² Nichols and Merritt: *Phys. Rev.*, (2) **9**, 113 (1917).

By means of the method described in this paper, it is possible to determine the exact composition and vapor pressure of all possible hydrates of a given substance, as well as to prepare each in a pure state for preservation and study. Whereas, most former methods have involved weeks and months for equilibrium to be attained at room temperature, this method yields results of equal accuracy in one to three hours. This has been proven by a study of $\text{BaCl}_2 \cdot 2-1 \text{ H}_2\text{O}$, which all who have tried, agree reaches equilibrium with extreme difficulty.

II. Previous Investigations

A very excellent summary with complete literature references to all work done on vapor pressures of hydrates up to 1921 is given by R. E. Wilson,¹ and will accordingly not be repeated here. The two methods which have usually been used may be classified as static and dynamic. A third method, known as indirect, has by far the greatest possibilities. The following objections may be raised against both the static and the dynamic methods. First, many hydrates approach equilibrium with extreme slowness when left undisturbed in a closed space. Some are not in equilibrium even after three or four months. Second, equilibrium is usually approached from one side only, and it is then difficult to ascertain how closely we have come to it. In addition to the above, the static method has the following objections. First, no satisfactory confining liquid is available. Mercury necessitates measurements of minute distances, while oil gives off gases slowly, and tends to dissolve and transmit water. Second, the presence of adsorbed (and occluded) gases on the surface of the hydrate, which is usually in a fine state of subdivision. These cannot usually be entirely removed in the pre-treatment, without destroying the hydrate at the same time. The indirect method, used by Mueller-Erzbach,² Tammann,³ van Bemmelen,⁴ Löwenstein,⁵ and Wilson,⁶ consisted in the determination of the concentration of sulfuric acid over which a pair of hydrates neither gained nor lost weight. By this method they arrived at the vapor pressure of the higher hydrate of the pair under consideration. Since the vapor pressure-concentration curve for sulfuric acid is well known, reference to it enables us to know the exact values of pressure over a solution of given concentration or density. Wilson recalculates and tabulates the best values for the vapor pressure of sulfuric acid at different temperatures and concentrations.

III. Micro Method for the Determination of Water of Hydration

Description of the Method. In a micro method involving weights, one of the prime essentials is a sensitive and accurate means for measuring differences in weight. In this method use was made of a very sensitive assay

¹ J. Am. Chem. Soc., 43, 704 (1921).

² Mueller-Erzbach: Ber., 14, 1093 (1881); Z. physik. Chem., 2, 113, 546 (1888); 4, 1 (1889); Wied. Ann., 32, 316 (1888).

³ Tammann: Ann. Chim. Phys., 63, 16 (1897); Z. physik. Chem., 27, 323 (1898); Wied. Ann., 33, 322 (1898).

⁴ Van Bemmelen: Z. anorg. Chem., 13, 233 (1897).

⁵ Löwenstein: Z. anorg. Chem., 63, 69 (1909).

⁶ Wilson: J. Am. Chem. Soc., 43, 704 (1921).

balance. (Johannes Meissner, Dresden). The whole balance case, except for the front sliding door, was practically air tight. The front door was so made that with very little extra effort it could be closed tightly. The bottom of the door was felt-lined. After closing the door, small wedges of wood were inserted to force it firmly against the felt lining in which it traveled.

A small hook made out of copper wire was fastened by means of wax to the inside top of the balance. From this was suspended an accurate thermometer. Two small microscope cover glasses (tared) were placed on the metal balance pans. To obviate the necessity of opening and closing the balance case during a determination, riders were arranged to serve in registering the loss or gain in weight. Since small samples were used (never over fifty milligrams), it was found that a ten-milligram rider on the left hand scale, and a twelve-milligram rider on the right hand scale, together with the two one-milligram riders that are used for ordinary weighings, served the purpose for these determinations. These riders were carefully calibrated by actual weighing, and in this way, the exact weight for any position of the combination of riders was known.

In order to expose a large surface and hold the acid conveniently, large flat dishes such as would just fit into the balance case were made by cutting off 400 cc. beakers about two centimeters from the bottom, so that the edge of the dish would be well below the level of the balance pans. In this balance there was space for two such containers besides three crystallizing dishes. This arrangement gave the maximum speed for reaching equilibrium conditions.

The procedure used to determine the hydrates with this apparatus was as follows: a saturated water solution of the salt was made, and painted on one of the cover glasses. This assured a thin uniform film. The weight of sample crystallizing later could be determined by the concentration of the solution used. At first, a small brush was tried, but it was found that a small rubber policeman served much better, by being easier to manipulate and later clean, besides using less of the solution.

The system of riders was so arranged as to take care of as large a loss in weight as their movement would permit. The cover glass with the salt, just before beginning to crystallize, was placed on one pan and the other cover glass on the other pan to hold the weights, as well as to assure equal buoyancy, adsorption, etc. After a few trials, enough weights can be taken off at the beginning of a determination so that, after the excess water has evaporated and the hydrate begins to crystallize, all the weighing may be made with the riders. Equilibrium can then be approached from the other side by a slight dehydration of the hydrate and following the gain in weight when the system is again closed. By complete dehydration of the sample by the use of concentrated acid, the weight of the anhydrous salt is determined and the hydrate calculated. By systematically introducing sulfuric acid solutions of different strengths, the equilibrium point between the two hydrates can be approached. When near the equilibrium point, solutions of such concentration can be used so that alternately a solution of greater vapor

pressure and one of less than the hydrate is used, in this manner closing in on the equilibrium point fairly closely. This method besides giving the composition of the hydrates, will give the limits in specific gravity of the acid to use in preparing the pure hydrates. An approximation of the vapor pressure of the pair of hydrates is also obtained.

The actual data in Table I will illustrate the general procedure and give an idea of the time required for a single determination.

TABLE I
From the Saturated Solution to the Hydrate $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ at 25°C over
 20.91% H_2SO_4

| Interval in minutes | Weight in Mg. | Loss in weight Mg. | Interval in minutes | Weight in Mg. | Loss in weight Mg. |
|---------------------|---------------|--------------------|---------------------|---------------|--------------------|
| 0 | 33.79 | 0.00 | 6 | 26.16 | 1.21 |
| 5 | 32.79 | 1.00 | 7 | 24.95 | 1.21 |
| 5 | 31.79 | 1.00 | 7 | 23.74 | 1.21 |
| 4 | 30.79 | 1.00 | 7 | 22.53 | 1.21 |
| 6 | 29.79 | 1.00 | 7 | 21.32 | 1.21 |
| 4 | 28.58 | 1.20 | 12 | 19.69 | 1.63 |
| 5 | 27.37 | 1.21 | 75 | 19.69 | 0.00 |

Since the hydrate has not changed in weight during a period of seventy-five minutes, 19.69 mg. is the weight of the hydrate. The weight when completely dehydrated over concentrated H_2SO_4 and heated for thirty minutes at 100°C to constant weight is 7.85 mg. The weight of the $12\text{H}_2\text{O}$ calculated from the anhydrous salt is 19.80 mg., as compared to the experimental value of 19.69 mg. Assuming the possibility of a compound $\text{Na}_2\text{HPO}_4 \cdot 11\text{H}_2\text{O}$, the weight calculated from the anhydrous salt would be 18.80 mg. The accuracy is accordingly such as to make it impossible to be in error by one molecule of water.

TABLE II
Hydrates of Na_2HPO_4

| H_2SO_4 in sol. % | Constant Wt. Mg. | Calc. from anhyd. salt | Wt. when dehydrated | Hydrate |
|-----------------------------------|------------------|------------------------|---------------------|-------------------------|
| 24.76 | 23.34 | 23.45 | 9.30 | 12 H_2O |
| 29.82 | 15.46 | 15.40 | 8.16 | 7 H_2O |
| 32.50 | 17.37 | 17.25 | 9.14 | 7 H_2O |
| 37.00 | 17.27 | 17.18 | 9.10 | 7 H_2O |
| 45.50 | 13.44 | 13.41 | 10.70 | 2 H_2O |

To get each of these values, a table similar to Table I was constructed, and the rate at which each hydrate was losing weight was closely followed.

To approximate the equilibrium point between the two hydrates, and get an estimate of the vapor pressure, the following procedure was adopted. When a sample of the hydrate pair $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} - 7\text{H}_2\text{O}$ was placed in

the presence of a 27.00% H_2SO_4 solution at 25°C, it lost weight, going in the direction of $\text{Na}_2\text{HPO}_4 \cdot 7 \text{H}_2\text{O}$. When a sample of the same hydrate pair was placed in the presence of 26.14% H_2SO_4 solution at 25°C, it gained in weight, going in the direction of $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$. The vapor pressure corresponding to 26.14% H_2SO_4 is 19.27 mm. Hg and that corresponding to 27.00% H_2SO_4 is 18.97 mm. Hg. Since the rate of approach to equilibrium was about the same from both sides, we can, to a first approximation take the average as the true value. The value obtained is 19.12 mm., as compared to 19.13 mm. given by Wilson from Dickinson's determinations. By varying the acid concentrations, a more exact value can readily be obtained.

Barium chloride was also tried because vapor pressure investigators all declare it to be difficult to determine. Only two concentrations of sulfuric acid were made up, and of such percentages as to fall on each side of the equilibrium point, according to Wilson's data.

Over the 55.00% acid the salt crystallized from the saturated solution and stable conditions were reached within an hour.

| | |
|----------------------------------------------|-----------|
| Constant weight | 13.34 mg. |
| Weight when dehydrated | 11.40 mg. |
| This calculated for $2\text{H}_2\text{O}$ is | 13.37 mg. |

The salt was then dehydrated half way between the 1 H_2O and the 2 H_2O . In two hours a gain in weight could be noticed.

Over 57.75% acid, when partially dehydrated, it lost weight. The vapor pressure of 55.00% acid at 25°C is 6.35 mm. Hg. The vapor pressure of 57.75% acid at 25°C is 5.05 mm. Hg. Wilson obtains the value of 5.8 mm. which is seen to be about the average of the above determinations. As before noted, the present determinations were made in much less time than Wilson's.

These results leave no doubt but what the conditions for the preparation of hydrates can be determined by this method in a reasonable time.

To adapt this method to accurate vapor pressure determination, the whole balance should be placed in a case capable of being closed tightly and having thermostatic temperature control.

IV. Method of Preparing and Preserving Pure Hydrates

Once the vapor pressure of a given hydrate pair is known, the higher of the two hydrates may be prepared as follow. A water solution or one of the solid hydrates is placed in one branch of a gas tight system and a large volume of sulphuric acid having a vapor pressure just above that of the desired hydrate is placed in another branch. The volume of the acid should be such that the small amount of water taken up by, or liberated by the hydrate will not change its concentration appreciably. The system may then be partially evacuated, and allowed to stand as long as necessary for equilibrium to be reached. Due to the partial vacuum, the tube containing the hydrate may then easily be sealed off by means of a blow torch.

V. Application of the Micro Method to the Determination of the Heat of Hydration

If we have determined the vapor pressure of a given hydrate pair at two temperatures close enough together for us to make the assumption that the heat of hydration is constant over the interval, we may proceed to calculate the heat by the method of Frowein.¹ The familiar Clausius-Clapeyron equation

$$\frac{d \ln p}{dT} = \frac{q}{RT^2}$$

applied to the dissociation of a hydrate would be interpreted as follows. q is the heat of dissociation of a gaseous molecule of the hydrate and p is the pressure of water vapor from the hydrate. Since we have a solid dissociating, we must also write the following equation for the heat of vaporization of water, where L represents the latent heat, and p_w the vapor pressure of pure water:

$$\frac{d \ln p_w}{dT} = \frac{L}{RT^2}$$

Subtracting the latter equation from the former, we have

$$\frac{d \ln p/p_w}{dT} = \frac{q - L}{RT^2}$$

Letting the ratio $p:p_w$ be represented by F and integrating we have

$$Q = q - L = \frac{R T_1 T_2}{T_1 - T_2} \ln \frac{F_1}{F_2}$$

The difference $(q - L) = Q$ represents the actual heat of hydration or dissociation measured calorimetrically. Determined in this manner by means of exact vapor pressures, the accuracy probably exceeds the direct determination.

Summary

1. In this article is described a micro method for the determination of the water of hydration of hydrates, which at the same time, gives the conditions for their preparation and preservation.
2. The method consists in introducing solutions of sulfuric acid in dishes in the tightly closed case of a very sensitive assay balance, with the sample painted from a saturated solution of the salt in the form of a thin film on a tared microscope cover glass. By means of riders of different weights, the loss or gain in weight, and finally the equilibrium weight is accurately known.
3. Data are given using disodium phosphate and also barium chloride showing this to be a simple and accurate method for the determination of the hydrates.

¹ Frowein: Z. physik. Chem., 1, 5 (1887).

4. Only very small samples are needed, and these are not lost, making this method especially applicable to costly and rare salts.
5. By this method an approximate idea of the vapor pressure is also obtained which can be increased in accuracy at will.
6. An adaptation of this method for accurate vapor pressure determinations, with only slight modifications, is described.
7. A method for the preparation and preservation of the pure hydrates is described.
8. The method whereby vapor pressures determined in this way may be applied to the determination of heats of hydration is given.

ADSORPTION OF MIXTURES OF EASILY CONDENSABLE GASES*

BY SIMON KLOSKY AND LEO P. L. WOO**

Extensive investigations have been undertaken on the adsorption of single gases in porous bodies such as charcoal, meerschaum, pumice, etc. Silica gels have been used by Patrick and others for the adsorption of sulfur dioxide,¹ butane,² etc. Burggraff³ was the first who used titania gel for adsorption purposes. Very few attempts have been made to investigate the adsorption of mixed gases. The investigations of Joulin,⁴ Miss Homfray,⁵ Bergter,⁶ Hempel and Vater,⁷ and Lemon and Blodgett⁸ were largely qualitative and were quantitative only when measuring the total volume adsorbed. Richardson and Woodhouse⁹ were the first investigators who studied the adsorption of carbon dioxide and nitrous oxide by charcoal by the static method and analysed for the composition of the adsorbed gas at different percentages. These two authors concluded from their experiments that "it seems possible to deduce the total amount of any mixture of carbon dioxide and nitrous oxide adsorbed by charcoal if the isotherms of the independent adsorption of the individual gases are known. The formula

$$V (\text{mix}) = \frac{a_1 V_{\text{SO}_2} + a_2 V_{\text{N}_2\text{O}}}{100}$$

in which V_{SO_2} and $V_{\text{N}_2\text{O}}$ represent the volumes of those gases separately adsorbed at the total pressure of the mixture and a_1 and a_2 stand for the percentages of the respective gases in the mixture, holds within certain limits. On the other hand, there seems to be no possibility of calculating the volume of each of the component gases adsorbed in the charcoal from the volume of the gaseous mixture. In other words the ratio of the amounts of the two gases adsorbed varies with the pressure whether we are dealing with them separately in contact with the charcoal or whether they are mixed."

It was the purpose of this investigation to measure at ordinary temperature the adsorption of mixtures of easily condensable gases such as sulfur dioxide, methyl chloride, butane, etc., by titania gel which was first prepared by

*Contribution from the Martin Maloney Chemical Laboratory, of the Catholic University of America.

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¹ Patrick and McGavack: *J. Am. Chem. Soc.*, **42**, 946 (1920).

² Patrick and Long: *J. Phys. Chem.*, **29**, 336 (1925).

³ Burggraff and Klosky: *J. Am. Chem. Soc.*, **50**, 1045 (1928).

⁴ Joulin: *Ann. Chim. Phys.*, (4) **37**, 472 (1912).

⁵ Homfray: *Z. physik. Chem.*, **74**, 129 (1910).

⁶ Bergter: *Ann. Physik*, (4) **37**, 472 (1912).

⁷ Hempel and Vater: *Z. Elektrochemie*, **18**, 724 (1912).

⁸ Lemon and Blodgett: *Phys. Rev.*, (2) **14**, 394 (1919).

⁹ Richardson and Woodhouse: *J. Am. Chem. Soc.*, **45**, 2638 (1923).

Klosky and Marzano,¹ in this laboratory and to determine the amounts of adsorbed gases in the gel with the hope of establishing some relationship between them.

Materials, Apparatus and Procedure

Titania gel. The gel was prepared by Burggraff. The particles of the gel were 20-40 mesh size. It was activated at 300°-330° C before use. The weight of gel used for each single determination was 4-5 gms. Two different samples of gel were used for the two systems.

The gases were purchased in tanks from a commercial company. The sulfur dioxide, after being dried, was found 99.6-99% adsorbable in NaOH solution. The butane was dried and purified according to the method employed by Patrick and Long. Kerosene was found suitable for adsorbing butane quantitatively. Methyl chloride was passed through NaOH solution and dried by calcium chloride. It was found 99.4-99% adsorbable by glacial acetic acid.²

Apparatus and procedure: All the determinations were made by a dynamic method similar to that used by Patrick and Opdyke,³ and described by Burggraff. The chief advantage of the dynamic method over the static one is that the former requires no exclusion of air and is more rapid although it is not as accurate as the latter at lower pressures. The total pressure was always equal to the atmospheric pressure. The individual isotherms of each gas were determined by mixing with air. The composition of the mixtures was determined first by flowmeters and then checked by the analysis from the bottle. The analysis was carried out either by titration as in the case of sulfur dioxide or by adsorption as in the case of butane or methyl chloride. The flowmeters were calibrated with air and when the reading of the flowmeter, measuring the gas, was multiplied by the relative viscosity of the gas compared to air, the per cent by volume calculated from these readings agreed with the results of analysis within 1.5% in all cases. The time required for the equilibrium was from 1 to 2.5 hours depending upon the pressures used. In every case a constant weight was obtained before changing the concentration of the gaseous mixtures. In the determination of independent isotherms one sample of gel was used for several different partial pressures. The partial pressures of the gas were changed from lower to higher in order to avoid the error due to the irreversibility of adsorption.

Analysis of Gases

As was mentioned above, the composition of each gas when mixed with air in the determination of individual isotherms was determined by analysis. The mixture of sulfur dioxide and air was analysed by the iodine method and also by adsorption in NaOH solution. Both methods checked closely. The mixture of butane and air and of methyl chloride were determined by absorption in kerosene and glacial acid respectively.

¹ Klosky and Marzano: *J. Phys. Chem.*, 29, 1125 (1925).

² Meighan: *J. Ind. Eng. Chem.*, 11, 943 (1919).

³ Patrick and Opdyke: *J. Phys. Chem.*, 29, 601 (1925).

The analysis of the mixtures of gases adsorbed in the gel presented great difficulties. It is impossible in the dynamic method to determine the composition of the adsorbed gases in the gel by knowing that of the unadsorbed gases, as in the case of the static method. The direct analysis of the adsorbed gases is necessary. After many trials it was found that the following method gave satisfactory results.

The U-tube containing the gel, after constant weight was obtained, was connected to a separatory funnel in which a known volume of standardized NaOH solution was placed. The solution was carefully run into the gel and then the gel was washed into a beaker. It was found that the concentration of the NaOH solution should be above .5N; when .1- .35 N solutions were used, only about 66.6% of the sulfur dioxide could be obtained. The solution containing the gel was warmed for about three minutes and then the excess of the NaOH was titrated as soon as possible by a standard solution of nitric acid, using phenolphthalein as indicator. Warming was also necessary, otherwise the error became as high as 33.0%. When the weight of the gases adsorbed and the amount of sulfur dioxide are known, the amount of the second component such as butane or methyl chloride can be readily calculated.

Experimental Results

Since Burggraff has already shown that the adsorption of sulfur dioxide by titania gel agrees very well with the equations of Freundlich, Patrick, and Polanyi, the adsorption of sulfur dioxide in this experiment was made at only one temperature, while those of butane and CH₃Cl were made at different temperatures. In Tables I-VII

P = pressure in atmospheres

x/m = grams of gas adsorbed per gram of gel

Experimental Data

TABLE I
Sulfur dioxide in gel No. 1
at 35° C.

| P(atm.) | x/m |
|---------|-------|
| .122 | .0358 |
| .431 | .0497 |
| .605 | .0543 |
| .995 | .0632 |

TABLE II
Sulfur dioxide in gel No. 2
at 35° C.

| P(atm.) | x/m |
|---------|-------|
| .194 | .0346 |
| .257 | .0373 |
| .478 | .0428 |
| .766 | .0478 |
| 1.000 | .0510 |

TABLE III
Butane in gel No. 1 at 0° C.

| P(atm.) | x/m |
|---------|-------|
| .122 | .0323 |
| .401 | .0562 |
| .610 | .0882 |
| .758 | .1065 |
| .796 | .1040 |
| 1.000 | .1340 |

TABLE IV
Butane in gel No. 1 at 35° C.

| P(atm.) | x/m |
|---------|-------|
| .100 | .0173 |
| .249 | .0206 |
| .332 | .0249 |
| .470 | .0293 |
| .625 | .0330 |
| .980 | .0395 |

| TABLE V CH ₂ Cl in gel No. 2 at 25°C. | | TABLE VI CH ₂ Cl in gel No. 2 at 35°C. | | TABLE VII CH ₂ Cl in gel No. 2 at 45°C. | |
|--------------------------------------------------------|-------|---------------------------------------------------------|-------|----------------------------------------------------------|-------|
| P(atm.) | x/m | P(atm.) | x/m | P(atm.) | x/m |
| .182 | .0369 | .150 | .0346 | .203 | .0305 |
| .427 | .0473 | .206 | .0324 | .486 | .0398 |
| .788 | .0683 | .570 | .0440 | .885 | .0474 |
| 1.000 | .0875 | .790 | .0519 | 1.000 | .0493 |
| | | 1.000 | .0558 | | |

In the mixture of gases it was found most desirable to plot the number of moles against the partial pressures. In Tables VIII-IX x_1 and x_2 represent the weight of gas adsorbed per gram of gel, the subscripts 1 and 2 indicate the first and second components of the gaseous mixture.

| TABLE VIII Sulfur dioxide-butane in titania gel No. 1 at 35°C. | | | |
|-------------------------------------------------------------------|-------|-------------------------------------|----------------------------------------------------|
| % SO ₂ | x | (x ₁)(SO ₂) | (x ₂)(C ₄ H ₁₀) |
| 0 | .0393 | .0000 | .0393 |
| 11.1 | .0445 | .0175 | .0270 |
| 14.0 | .0443 | .0228 | .0215 |
| 24.4 | .0474 | .0298 | .0176 |
| 49.2 | .0505 | .0360 | .0145 |
| 77.0 | .0578 | .0448 | .0130 |
| 100.0 | .0625 | .0625 | .0000 |

| TABLE IX Sulfur dioxide-methyl chloride in titania gel No. 2 at 25°C. | | | |
|--------------------------------------------------------------------------|-------|-------------------------------------|---------------------------------------|
| % SO ₂ | x | (x ₁)(SO ₂) | (x ₂)(CH ₂ Cl) |
| 0 | .0558 | .0000 | .0558 |
| 13.5 | .0585 | .0193 | .0392 |
| 23.1 | .0600 | .0235 | .0365 |
| 29.6 | .0605 | .0274 | .0331 |
| 42.3 | .0590 | .0298 | .0292 |
| 64.0 | .0578 | .0374 | .0204 |
| 79.2 | .0545 | .0405 | .0140 |
| 81.5 | .0535 | .0407 | .0128 |
| 100.0 | .0510 | .0510 | .0000 |

Discussion of Results

The data on the adsorption of single gases have been used to test the equations of Freundlich, Patrick, and Polanyi and found to agree fairly well.

The interesting qualitative discussion of Drucker¹ about the close relationship between viscosities and adsorption of mixtures of gases induced

¹ Drucker: Z. physik. Chem., 92, 287 (1917).

us to make an attempt to find some quantitative connections among them. It was found that the ratio of the molecular weights and viscosities of sulfur dioxide and butane is 1.80 which is almost exactly equal to the inverse ratio of the relative adsorption lowering of the two gases.

In Tables X-XI N and N' represent respectively the number of mols of the first and second components of the gases adsorbed per gram of gel from the mixtures. The subscript zero represents the corresponding amounts adsorbed from the gas-air mixtures.

TABLE X
Sulfur dioxide-butane, at 35° C.

| % | N_0 | N_0' | N | N' | $\frac{N_0-N}{N_0}$ | $\frac{N_0'-N'}{N_0'}$ | $\frac{N_0'-N'}{N_0'}/\frac{N_0-N}{N_0}$ |
|----|---------|---------|---------|---------|---------------------|------------------------|------------------------------------------|
| 20 | .000614 | .000305 | .000431 | .000165 | .298 | .522 | 1.75 |
| 40 | .000760 | .000643 | .000540 | .000228 | .290 | .509 | 1.76 |
| 60 | .000860 | .000555 | .000615 | .000256 | .286 | .539 | 1.87 |
| 80 | .000940 | .000625 | .000718 | .000350 | .236 | .440 | 1.86 |
| | | | | | Average | | 1.81 |

TABLE XI
Sulfur dioxide-methyl chloride, at 35° C.

| % | N_0 | N_0' | N | N' | $\frac{N_0-N}{N_0}$ | $\frac{N_0'-N'}{N_0'}$ | $\frac{N_0'-N'}{N_0'}/\frac{N_0-N}{N_0}$ |
|----|---------|---------|---------|---------|---------------------|------------------------|------------------------------------------|
| 20 | .000547 | .000620 | .000360 | .000275 | .342 | .555 | 1.62 |
| 40 | .000643 | .000770 | .000475 | .000470 | .262 | .390 | 1.48 |
| 60 | .000710 | .000900 | .000567 | .000623 | .201 | .307 | 1.53 |
| 80 | .000755 | .001010 | .000632 | .000744 | .163 | .263 | 1.61 |
| | | | | | Average | | 1.56 |

These data are shown graphically in Figs. 1-2.

The values of viscosities are taken from Landolt-Börnstein's Tabellen at 20°C since those at 35°C are not all available. We may also note that the ratio of viscosities does not vary appreciably with temperature, so no considerable error would occur when we use the ratio of viscosities at 20°C. for that at 35°C. The same procedure can be applied to the sulfur dioxide-methyl chloride system, where the average ratio is 1.53 as shown in Col. 8, Table XI. The inverse ratio of the molecular weights and viscosities of sulfur dioxide and methyl chloride is:

$$\frac{M_1\eta_1}{M_2\eta_2} = \frac{64(1380)(10)^{-7}}{50.5(1160)(10)^{-7}} = 1.51$$

If we use the equation

$$\frac{\frac{N_0-N}{N_0}}{\frac{N_0'-N'}{N_0'}} = \frac{M_2\eta_2}{M_1\eta_1} \quad (1)$$

to calculate the second component from the two independent isotherms and from the first component, a surprising agreement between the calculated and observed values is obtained as is shown in Table XII-XIII.

| Table XII | | | | TABLE XIII | | |
|-------------------------|---------|----------|---------|----------------------------------|----------|---------|
| N ₂ = butane | | | | N ₂ = methyl chloride | | |
| % | N(obs.) | N(calc.) | % error | N(obs.) | N(calc.) | % error |
| 20 | .000165 | .000160 | 3.0 | .000275 | .000296 | -7.1 |
| 40 | .000228 | .000221 | 3.3 | .000470 | .000464 | 0.6 |
| 60 | .000256 | .000252 | 1.6 | .000623 | .000626 | -0.5 |
| 80 | .000350 | .000359 | -2.5 | .000744 | .000764 | -2.8 |
| Average | | | 2.6 | Average | | 2.8 |

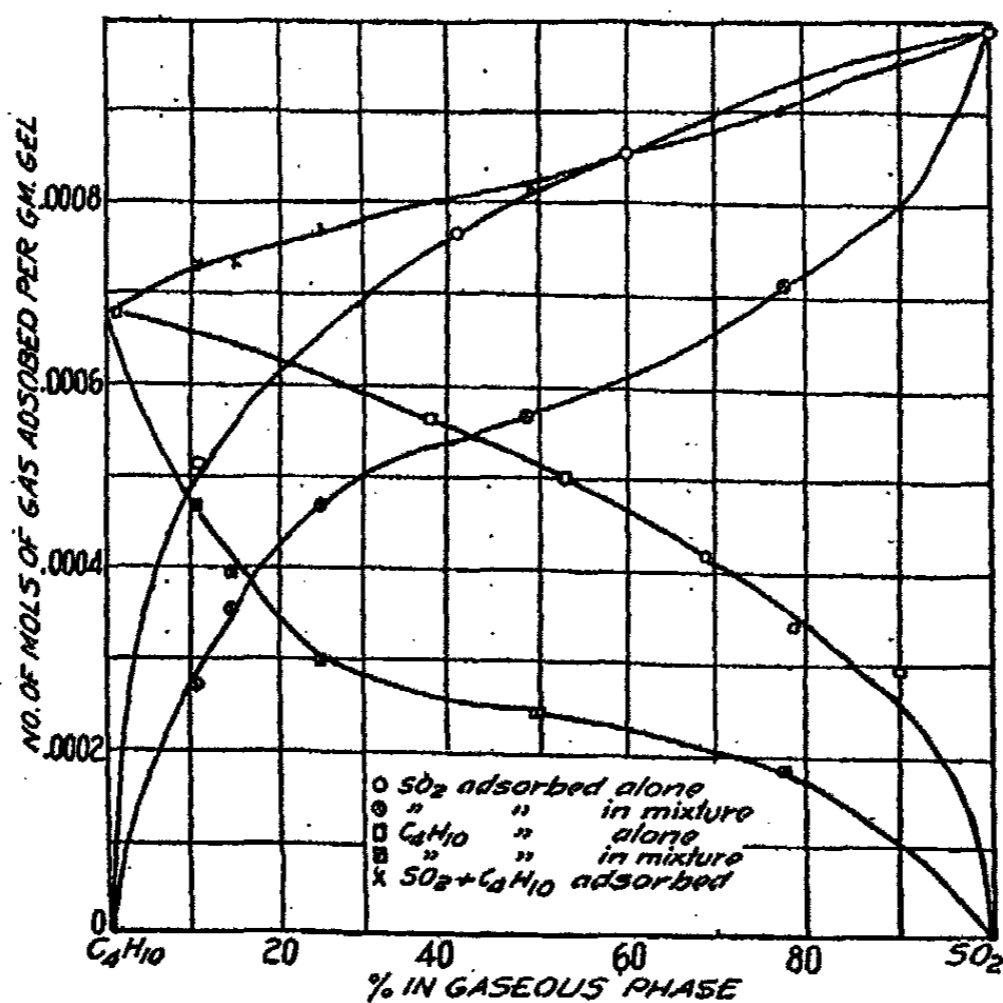


FIG. 1
SO₂-C₄H₁₀

In going over the data of Richardson and Woodhouse it was unusually interesting to find that equation (1) again holds as well as could be expected. Their data were obtained from a static method. For the sake of comparison it was necessary to retabulate their results, that is, to plot volumes adsorbed against pressures. Curves were plotted on large scales according to Table XIV. The readings on Tables XV-XVII were obtained directly from the curves, and the agreement between the calculated and observed values are shown by the last columns of the three tables. The average per cent error is only 2.1-3.5.

TABLE XIV

| % | P (total) 1000 mm. | | P 2000 mm. | | P 3000 mm. | |
|------|--------------------|----------------|----------------|----------------|----------------|----------------|
| | V ₁ | V ₂ | V ₁ | V ₂ | V ₁ | V ₂ |
| 49.2 | 29.2 | | 40.7 | | 47.5 | |
| 50.8 | | 38.3 | | 48.6 | | 54.0 |
| 73.9 | 53.1 | | 72.5 | | 81.8 | |
| 26.1 | | 16.0 | | 20.5 | | 22.8 |
| 23.4 | 8.9 | | 13.5 | | 16.5 | |
| 76.6 | | 65.5 | | 81.6 | | 88.4 |
| 100 | 84.2 | 94.8 | 107.3 | 113.0 | 121.0 | 120.0 |

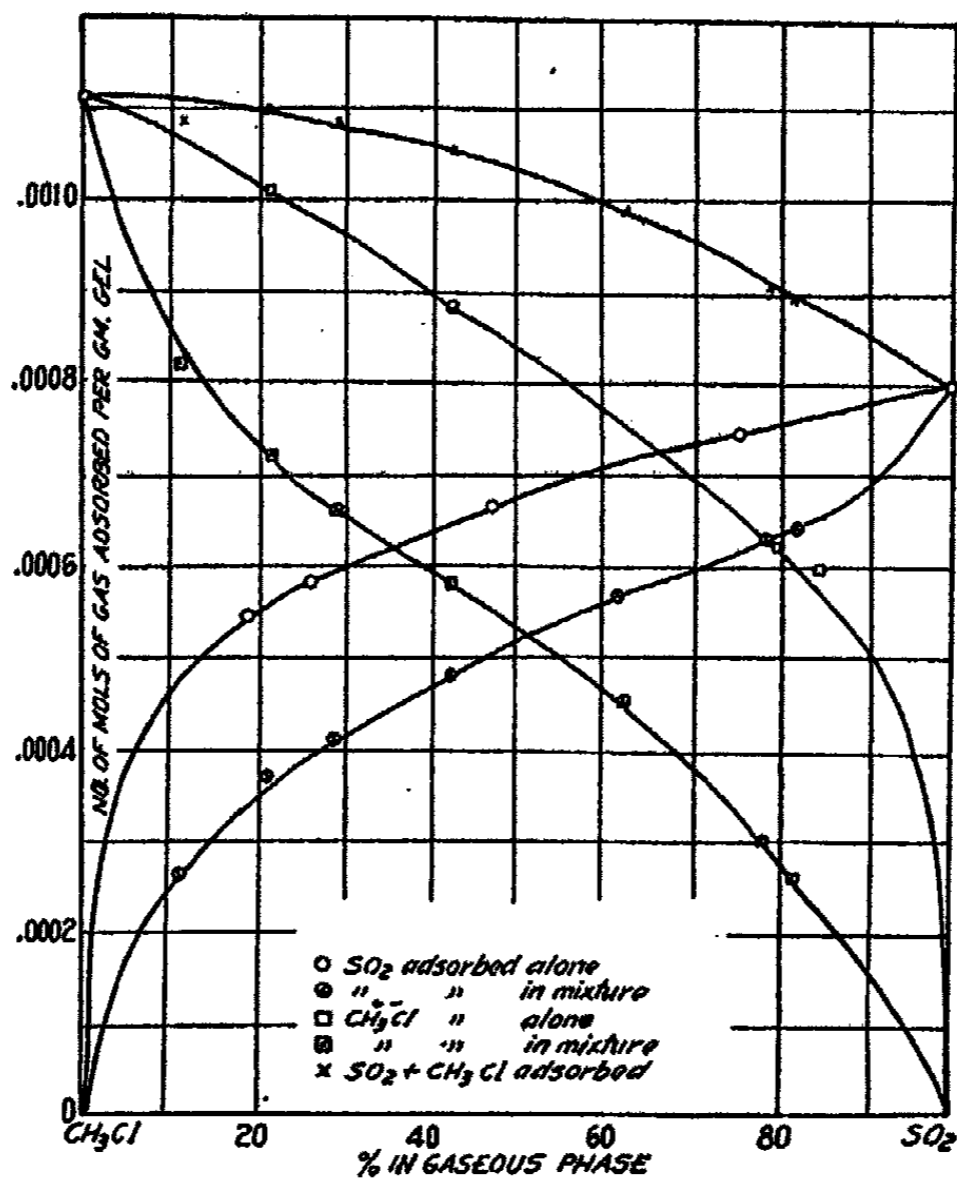


FIG. 2
SO₂-CH₂Cl

TABLE XV

When total P = 1000 mm.

| % | V(calc.) | V ₂ (obs.) | % error |
|----|----------|-----------------------|---------|
| 20 | 9.0 | 9.5 | 5.0 |
| 40 | 25.7 | 27.5 | 6.0 |
| 60 | 47.2 | 48.0 | 1.5 |
| 80 | 70.5 | 69.4 | -1.5 |
| | Average | | 3.5 |

TABLE XVI

When total P = 2000 mm.

| % | V(Calc.) | V ₂ (obs.) | % error |
|----|-----------|-----------------------|---------|
| 20 | 14.5 | 15.0 | 3.5 |
| 40 | 34.4 | 35.7 | 3.8 |
| 60 | 59.5 | 59.7 | 0.2 |
| 80 | 86.6 | 85.5 | -1.0 |
| | Average | | 2.1 |

TABLE XVII

| % | When the total P = 3000 mm. | | % error |
|----|-----------------------------|-----------------------|---------|
| | V(calc.) | V ₃ (obs.) | |
| 20 | 14.2 | 15.0 | 5.5 |
| 40 | 39.1 | 40.3 | 3.0 |
| 60 | 65.1 | 66.0 | 1.2 |
| 80 | 92.4 | 91.8 | -0.8 |
| | Average | | 2.6 |

The ratio of molecular weights and viscosities of CO₂ and N₂O is almost exactly equal to 1. Considering the fact that adsorption experiments are relatively difficult especially at low pressures, as it was stated by the authors themselves, "under the best conditions the amount of gas adsorbed by a given specimen of charcoal varies several cubic centimeters in duplicate determinations," we feel that the agreement is remarkably close. So far as we know, the data of Richardson and Woodhouse are the only ones in the literature on adsorption of mixtures of gases by porous bodies which are extensive enough to be tested. Lorenz and Wiedbrauck's¹ experiment on CO₂-C₂H₄ mixtures does not furnish any data on the actual amount adsorbed, while Magnus and Ruth's² experiment on CO₂-H₂ mixtures does not contain the individual adsorption isotherms. Hence these data cannot be used to test our equation. Again let us consider the experiments of Richardson and Woodhouse and ours: the methods, gases, adsorbents, temperatures and total pressures are entirely different, yet all of them can be represented by the simple equation. Hence, it is very probable that molecular weights and especially viscosities of the components play an important part in the complicated phenomena of adsorption of gases by, at least, porous bodies.

It may be well to point out that the formula

$$V(\text{mix}) = \frac{V_{1a_1} + V_{2a_2}}{100}$$

which has been used by Homfray, Richardson and Woodhouse, and others holds in our SO₂-C₄H₁₀ system. Let us change the form of the equation into

$$N(\text{mix}) = \frac{N_{1a_1} + N_{2a_2}}{100}$$

where N indicates number of mols and the subscripts indicate the first and second components. The agreement is shown in Table XVIII. The equation does not hold even roughly in the case of the SO₂-CH₂Cl system.

¹ Lorenz and Wiedbrauck: *Z. anorg. allgem. Chem.*, 143, 268 (1925).

² Magnus and Ruth: *Z. anorg. allgem. Chem.*, 150, 311 (1926).

TABLE XVIII

| % | N (mix) (calc.) | N (mix) (obs.) | % error |
|------|-----------------|----------------|---------|
| 11.1 | .000711 | .000739 | 3.9 |
| 14.0 | .000720 | .000728 | 1.0 |
| 24.4 | .000753 | .000768 | 2.0 |
| 49.3 | .000829 | .000812 | -2.0 |
| 77.0 | .000916 | .000985 | 7.0 |
| | | Average | 3.5 |

Summary

1) Adsorption isotherms of C_4H_{10} at $0^\circ C$ and $25^\circ C$, and CH_3Cl at $25^\circ C$, $35^\circ C$ and $45^\circ C$ on titania gel have been determined and found to agree with the formulae of Freundlich, Patrick, and Polanyi.

2) The adsorption of mixtures of SO_2 plus CH_3Cl , and SO_2 plus C_4H_{10} by titania gel have also been measured.

3) A simple formula has been proposed which holds for all available data with an average deviation of approximately three per cent.

FORMULAE FOR THE INTERNAL ENERGY AND ENTROPY OF A SUBSTANCE OR MIXTURE

BY R. D. KLEEMAN

In a previous paper the writer showed¹ that the controllable internal energy u and the controllable entropy S are each zero for a substance or mixture in the condensed state under its vapor pressure at the absolute zero of temperature, a point called the absolute zero of control, or

$$S = 0 \quad (1)$$

$$u = 0 \quad (2)$$

under these conditions. It was also shown² that the entropy is also zero for all other states at the absolute zero of temperature. If we make use of the postulates already used in the first paper quoted, that $\left(\frac{\partial S}{\partial T}\right)_v$ and $\left(\frac{\partial S}{\partial v}\right)_T$ are not discontinuous for a homogeneous mass of matter of volume v and absolute temperature T , it will follow from the foregoing result by means of the Calculus that

$$\left(\frac{\partial S}{\partial T}\right)_v = 0 \quad (3)$$

$$\left(\frac{\partial S}{\partial v}\right)_T = 0 \quad (4)$$

for all states of matter at the absolute zero of temperature. From these equations it can then be deduced, similarly as in the papers quoted for the case that the substance is under its vapor pressure, that

$$\left(\frac{\partial u}{\partial T}\right)_v = c_v = c_{v\infty} = 0 \quad (5)$$

$$\left(\frac{\partial^2 u}{\partial T^2}\right)_v = \left(\frac{\partial c_v}{\partial T}\right)_v = \left(\frac{\partial c_{v\infty}}{\partial T}\right)_v = 0 \quad (6)$$

$$\left(\frac{\partial p}{\partial T}\right)_v = 0 \quad (7)$$

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0 \quad (8)$$

for all states of matter under any given pressure at $T = 0$, where c_v denotes the specific heat of the condensed substance at constant volume, $c_{v\infty}$ the specific heat at constant infinite volume of the vapor, and p the pressure.

Again, since the entropy is zero for $T = 0$

$$\frac{L + w}{T} = 0,$$

¹ J. Phys. Chem., 31, 747 (1927).

² J. Phys. Chem., 31, 940 (1927).

where L denotes the internal heat of evaporation, and w the work done during evaporation. It follows therefore that

$$-L = w = p(v_2 - v_1) = RT = 0 \quad (9)$$

where v_2 denotes the volume of the vapor and v_1 that of the condensed substance.

The discussion of the foregoing results together with others will be reserved for a separate paper; in this paper they will be used mainly to develop formulae for the internal energy and entropy. Considerable use will also be made of the well known equation

$$\left(\frac{\partial u}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - p \quad (10)$$

1. Formulae for the Controllable Internal Energy of a Substance or Mixture

Since the internal energy of a substance corresponding to a given state is independent of the path along which this state may be reached from the zero of internal energy, an infinite number of formulae for the internal energy may be deduced. A few of them only are however of interest and importance, and these will now be given.

Suppose that a substance at the absolute zero of temperature under the pressure of its vapor, in which case its controllable internal energy is zero, has its temperature increased to T at constant volume v_0 . The increase in internal energy is

$$\int_0^T c_{v_0} \cdot \partial T$$

where c_{v_0} denotes the specific heat at the constant volume v_0 . Next suppose that the volume is isothermally increased from v_0 to v . The increase in

internal energy is $\int_{v_0}^v \partial u$, which may be written

$$\int_{v_0}^v \left\{ T \left(\frac{\partial p}{\partial T}\right)_v - p \right\} \partial v$$

by means of equation (10). It is evident from equations (5) and (6) that the integral corresponding to the limit $T = 0$ is zero; and hence for the internal energy u we have

$$u = \int_0^T c_{v_0} \cdot \partial T + \int_{v_0}^v \left\{ T \left(\frac{\partial p}{\partial T}\right)_v - p \right\} \partial v \quad (11)$$

We may also proceed by supposing that the substance in the same initial state as before is allowed to evaporate giving rise to an increase in internal energy equal to the internal heat of evaporation L , which according to equation (9) is zero. On next supposing that the temperature is increased to T at constant infinite volume an increase in internal energy equal to

$$\int_0^T c_{v_\infty} \cdot \partial T$$

is obtained, where c_{v_∞} denotes the specific heat at constant infinite volume v_∞ . Finally on supposing that the volume of the substance is isothermally decreased from v_∞ to v , an increase

$$\int_{v_\infty}^v \left\{ T \left(\frac{\partial p}{\partial T} \right)_v - p \right\} \partial v$$

in internal energy is obtained. The integral corresponding to $T = 0$ is zero according to equations (5) and (6), and hence for the internal energy we have

$$u = \int c_{v_\infty} \cdot \partial T + \int_{v_\infty}^v \left\{ T \left(\frac{\partial p}{\partial T} \right)_v - p \right\} \partial v \quad (12)$$

The relation between c_v and c_{v_∞} at any temperature obtained before¹ is

$$c_{v_\infty} - c_v = T \int_v^{v_\infty} \left(\frac{\partial^2 p}{\partial T^2} \right)_v \cdot \partial v \quad (13)$$

An expression for the internal energy of a vapor in contact with its condensed state, which is convenient, is obtained on supposing that the substance in contact with its vapor is heated from $T = 0$ to T and then evaporated giving

$$u = \int c_i \cdot dT + L \quad (14)$$

where c_i denotes the internal specific heat of the condensed substance in contact with its vapor, and L the internal heat of evaporation at the temperature T .

Another expression for the internal energy is obtained on integrating the known equation

$$\left(\frac{\partial H}{\partial T} \right)_p = c_p \quad (15)$$

giving

$$u + pv = H = \int c_p \cdot \partial T + \Phi_0(p) \quad (16)$$

where c_p denotes the specific heat at constant pressure, and $\Phi_0(p)$ the integration function. If the specific heat is measured at an infinitely low pressure we have $\Phi_0(p) = 0$, since $u = 0, c_p = 0, p = 0$ when $T = 0$, and hence

¹ J. Phys. Chem., 31, 747 (1927)

² J. Phys. Chem., 31, 940 (1927).

$$u + pv = H = \int c_p \cdot \partial T \quad (17)$$

under these conditions. This equation also holds very approximately if p is not zero, but at the same time not very large, say of the order of an atmosphere or so; u can be calculated from this equation if the continuity temperature function of c_p is known. It is the function of T that represents the specific heat over the region of values of T that the substance is in one phase, and for all temperatures down to the absolute zero supposing the substance to remain continuous, or not condense into phases. This function depends on the same idea of continuity as introduced by van der Waals in connection with his equation of state, which has been shown to be permissible. Its form can be discovered by trial only and is not yet known, but its discovery should not present any insuperable difficulties. Very probably its form with respect to T will be found to be the same for all substances, while its constants would depend on the nature of the substance considered.

An expression for p in the foregoing internal energy equations in terms of v and T is given by the equation of state of the substance or mixture. It may be of an entirely empirical character provided its constants are determined from the facts. The value of v_0 , the volume of the substance under the pressure of its vapor at $T = 0$, according to Traube,¹ is given by

$$v_0 = 2.6 \sum N_a \sqrt{w_a} \quad (18)$$

where N_a denotes the number of gram atoms of the substance a of atomic weight w_a relative to the hydrogen atom the substance or mixture contains.

Another formula for the internal energy will now be obtained which can be developed along special lines. On multiplying equation (10) by ∂v and integrating, it becomes

$$u = \int \left\{ T \left(\frac{\partial p}{\partial T} \right)_v - p \right\} \partial v + \Phi_1 (T, M_a, M_b \dots) \quad (19)$$

where M_a, M_b, \dots denote respectively the number of gram atoms of the substances a, b, \dots the substance or mixture contains, and Φ_1 is the integration function. Now the part of the expression for u which varies with v is a

function of the partial densities $\frac{M_a}{v}, \frac{M_b}{v}, \dots$ of the constituents. Hence the

integration function in the equation will consist of two parts, one of which is a function of the partial densities and the temperature, and the other a function of the masses and the temperature. The expression for u will also possess the property that if the masses of the constituents are increased n times at constant pressure the value of the expression is increased n times. This is realized if the expression has the form

¹ Physik. Z., 10, 667 (1909).

$$u = M_a \cdot \psi_a \left(T, \frac{M_a}{v}, \frac{M_b}{v}, \dots \right) + M_b \cdot \psi_b \left(T, \frac{M_a}{v}, \frac{M_b}{v}, \dots \right) + \dots + M_n \cdot \phi_n (T) \\ + M_b \cdot \phi_b (T) + \dots$$

$$\text{or,} \quad u = \sum M \cdot \psi \left(T, \frac{M_a}{v}, \frac{M_b}{v}, \dots \right) + \sum M \cdot \phi (T) \quad (20)$$

The form of the expression for u need not always be the same for a given set of constituents. This is suggested by the existence of isomers. The complex substances which correspond to the same expression for u will be said to be of the same type.

If the masses of the constituents are supposed to be zero except one, equation (20) gives the internal energy of this constituent at the volume v and temperature T . The resultant equation is likely to be the same in most cases whatever the nature of the expression for u , and to correspond to the nature of the substance as it is known in practice. In some cases, however, the resultant equation may not have the same form, since different molecular forms of the same elementary substance may exist.

Similar considerations apply to the equation of state of a complex substance or mixture. It may be written in the general form

$$p = \phi_1 \left(T, \frac{M_a}{v}, \frac{M_b}{v}, \dots \right) \quad (21)$$

where the function ϕ need not always be the same for a given set of constituents. If we suppose that the masses of the constituents are zero except one in the foregoing equation—say a , it will give the equation of state of the remaining elementary substance a . But this need not always be the same in form since a substance in some cases may exist in different forms; the resultant equation refers to the form of the elementary substance taking part in the chemical combination.

A special form of equation (20) is obtained on applying it to substances in the gaseous state which do not dissociate appreciably on changing their volumes from v_1 to v_2 . The internal energy of each substance will accordingly not change appreciably over this range of volumes, and hence the functions of the type ψ are approximately independent of v under these conditions. They will therefore also be approximately independent of the masses of the constituents, since u is a function of the ratios $\frac{M_a}{v}, \frac{M_b}{v}, \dots$, if the mass of a constituent is not varied over a greater range than from 1 to v_2/v_1 . The expression for u under these conditions may be written

$$u = M_a \cdot \xi_a(T) + M_b \cdot \xi_b(T) \dots = \sum M \cdot \xi(T) \quad (22)$$

or u is an additive quantity of its constituents. This result applies only, from what has gone before, to substances of the same type.

It is evident from equation (20) that u is perfectly additive for compounds of the type $A_{na} B_{nb} \dots$ in the gaseous state independent of dissociation,

where a, b, \dots are constants, if the volumes are taken proportional to n , since in that case the relative partial densities of the constituents, or the values of $\frac{M_a}{V}, \frac{M_b}{V}, \dots$ are the same in each case.

Equation (22) may be tested by means of the equation

$$\Delta H = \Delta u + \Delta pv \quad (23)$$

applied to the facts, where ΔH denotes the change in heat content during a reaction, or the heat of combination or combustion as the case may be. If we are considering gases of the kind discussed Δu is additive and this holds also for Δpv except one or more terms each equal to RT , which may be neglected.

The writer has shown¹ that for the hydrocarbons (32 were considered) the heat of combustion $-(\Delta H)_0$ may be expressed by

$$-(\Delta H)_0 = 29500 (h + c \sqrt{12}) \text{ cal.} \quad (24)$$

or it is additive, where h denotes the number of gram atoms of hydrogen, and c the number of gram atoms of carbon, a gram molecule of a given hydrocarbon contains. We may also write

$$(\Delta H)_0 = c \cdot u_{cO_2} + \frac{h}{2} u_{H_2O} - u_{c_0H_h} - (c + \frac{h}{4}) u_{O_2} - (1 + \frac{h}{4}) RT \quad (25)$$

where $u_{c_0H_h}$ denotes the internal energy of the hydrocarbon per gram molecule in the gaseous state, u_{O_2} the internal energy of a gram molecule of oxygen in the gaseous state, and u_{H_2O} the internal energy of a gram molecule of liquid water, and

$$\Delta H_{CO_2} = u_{CO_2} - u_C - u_{O_2} \quad (26)$$

$$\Delta H_{H_2O} = u_{H_2O} - u_{H_2} - \frac{1}{2} u_{O_2} - \frac{1}{2} RT \quad (27)$$

where u_{CO_2} and u_{H_2} denote the internal energies of gram molecules of carbon dioxide and hydrogen in the gaseous state, and u_C the internal energy of a gram atom of graphite. From the foregoing four equations we have

$$u_{c_0H_h} - cu_C - \frac{h}{2} u_{H_2} = c \{ \Delta H_{CO_2} + 29500 \sqrt{12} \} + h \left\{ \frac{1}{2} \Delta H_{H_2O} + 29500 + \frac{RT}{4} \right\} \quad (28)$$

where the left hand side of the equation represents the heat of formation from the elements. It is evident from this equation that the internal energy is an additive quantity of the atoms. The calculation of the factors of c and h in the foregoing equation cannot result in accurate values being obtained on account of each being the difference of two large quantities and that the constant 29,500 is an average value. Since in practice we are almost exclusively concerned with the value of Δu considered as a whole it is best to calculate it in each individual case by means of the equation

¹ Proc. Cambridge Phil. Soc., 16, (4), 299 (1911).

$$\Delta u = u_{C_2H_4} - c \cdot u_C - \frac{h}{2} u_{H_2} = c \Delta H_{CO_2} + \frac{h}{2} \Delta H_{H_2O} + (\Delta H)_C + \frac{h}{4} RT \quad (29)$$

The writer has also shown that the equation

$$\frac{-(\Delta H)_C + n 50700}{h + c \sqrt{12}} = 29500 \quad (30)$$

holds for the mon- and multiatomic alcohols, carbohydrates, phenols, aldehydes, ketones, basic and oxy-acids, comprising in all about 120 compounds, where n denotes the number of gram atoms of oxygen a gram molecule of a given compound contains. It can easily be shown from this that the internal energy is an atomic additive quantity.

In the case of the amido-acids, acid amido compounds, nitrile acids, and the uric acid group it was shown that

$$\frac{-(\Delta H)_C + n 50700 + m 5000}{h + c \sqrt{12}} = 29500 \quad (31)$$

where m denotes the number of gram atoms of nitrogen a gram molecule of a compound contains. As before this equation shows that an additive law holds for the internal energy.

The relation.

$$\frac{-(\Delta H)_C - m 7300}{h + c \sqrt{12}} = 29500 \quad (32)$$

was shown to hold for the amines, and the relation

$$\frac{-(\Delta H)_C - m 29500}{h + c \sqrt{12}} = 29500 \quad (33)$$

for the cyanides. The contribution of a nitrogen atom to the internal energy of a molecule, it will be seen, is not the same in the two cases.

For the iodides considered it was found that

$$\frac{-(\Delta H)_C - w 9400}{h + c \sqrt{12}} = 29500 \quad (34)$$

and for the bromides

$$\frac{-(\Delta H)_C + u 5800}{h + c \sqrt{12}} = 29500 \quad (35)$$

where w denotes the number of gram atoms of iodine and u the number of gram atoms of bromine a given gram molecule contains.

The larger number of chlorides considered fall into line with the equation

$$\frac{-(\Delta H)_C + t 13600}{h + c \sqrt{12}} = 29500 \quad (36)$$

where t denotes the number of gram atoms of chlorine a gram molecule contains. Similar relations were found to hold for other compounds involving various kinds of atoms. They indicate that the internal energy is an additive quantity when the substance is in the gaseous state, but the amount contributed by a given kind of atom depends sometimes on the type of compound in which it occurs. Thus the theoretical considerations given are amply

sustained by the facts. This is the more important because similar considerations will be applied to the entropy for the verification of which no data are at present available.

It may be noted however that since the foregoing grouping of compounds is only an approximation, it may be necessary when actually calculating the internal energy of compounds by its help to subdivide these groups into subsidiary groups. The nature of this subsidiary grouping will probably be found to be intimately connected with the grouping of the atoms of the molecules.

The formula (19) for the internal energy may be given another form which is of interest and importance. It may be written

$$u = \int \left\{ T \left(\frac{\partial p}{\partial T} \right)_v - p \right\} \partial v + \Phi(T, M_a, M_b, \dots) + \Sigma M \cdot \phi(T) \quad (37)$$

on comparing it with equation (20), where Φ is the function of T, M_a, M_b, \dots which renders the integral a series of functions of $T, \frac{M_a}{v}, \frac{M_b}{v}, \dots$ each of which has one of the quantities M_a, M_b, \dots as a factor, which is the series corresponding to $\Sigma M \cdot \psi(T, \frac{M_a}{v}, \frac{M_b}{v}, \dots)$ in equation (20). The form of this function Φ depends on the equation of state of the substance or mixture, from which it may immediately be deduced. If the masses of all the constituents except a are supposed to be zero the equation becomes

$$u_a = \int \left\{ T \left(\frac{\partial p}{\partial T} \right)_v - p \right\} \partial v + \Phi(T, M_a, 0, \dots) + M_a \cdot \phi_a(T) \quad (38)$$

and expresses the internal energy of the constituent a at the volume v and temperature T . It is evident now that the functions of the type $\phi(T)$ in equation (37) may be obtained from the equations referring to the elementary substances. We may therefore write

$$\Delta u = \Delta \int \left\{ T \left(\frac{\partial p}{\partial T} \right)_v - p \right\} \partial v + \Delta \Phi(T, M_a, M_b, \dots) \quad (39)$$

Hence if the correct equations of state of the complex substance and its constituents, and the internal energies of the constituents, be known, the internal energy of the complex substance may immediately be calculated.

If we suppose that equation (20) is applied to a complex substance or mixture at infinite volume the function $\psi(T, \frac{M_a}{v}, \frac{M_b}{v}, \dots)$ assumes the same form as if all the masses of the constituents were equal to zero except that of a , and the volume infinitely large, in other words, the function assumes the form applying to the isolated elementary substance a at infinite volume. Similar remarks apply to the other functions of this type. Thus at infinite volume u consists of the sum of the internal energies of the constituents when sepa-

rated from each other, in other words, no change in internal energy takes place on mixing a number of substances of the same type at infinite volume.

2. Formulae for the Controllable Entropy of a Substance or Mixture

The formulae for the entropy corresponding to the formulae (11), (12) and (14) given in the previous Section can easily be shown to be

$$S = \int \frac{c_{v_0}}{T} \cdot \partial T + \int_{v_0}^v \left(\frac{\partial p}{\partial T} \right)_v \cdot \partial v \quad (40)$$

$$S = \int \frac{c_{v_\infty}}{T} \cdot \partial T + \int_{v_\infty}^v \left(\frac{\partial p}{\partial T} \right)_v \cdot \partial v \quad (41)$$

$$S = \int \frac{c}{T} \cdot dT + \frac{L_v}{T} \quad (42)$$

where L_v denotes the total heat of evaporation, and the c the specific heat of the substance in contact with its vapor. Another formula may be obtained by integrating the well known equation

$$\left(\frac{\partial S}{\partial T} \right)_p = \frac{c_p}{T} \quad (43)$$

giving

$$S = \int \frac{c_p}{T} \cdot \partial T + \phi(p) \quad (44)$$

where $\phi(p)$ is the integration function. If the specific heat is measured at any given pressure $\phi(p)$ is zero, since $S = 0$, $c_p = 0$ and $\frac{\partial c_p}{\partial T} = 0$ when $T = 0$,¹ and hence

$$S = \int \frac{c_p}{T} \cdot \partial T \quad (45)$$

¹ $c_p = \left(\frac{\partial u}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p + \left(\frac{\partial u}{\partial T} \right)_v + p \left(\frac{\partial v}{\partial T} \right)_p = 0$ by means of equations (7) and (5)

and since $\left(\frac{\partial v}{\partial T} \right)_p = - \left(\frac{\partial v}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_v$.

Again $\left(\frac{\partial c_p}{\partial T^2} \right)_p = \left(\frac{\partial}{\partial T} \left(\frac{\partial u}{\partial v} \right)_T \right)_p \left(\frac{\partial v}{\partial T} \right)_p + \left(\frac{\partial u}{\partial v} \right)_T \left(\frac{\partial^2 v}{\partial T^2} \right)_p + \left(\frac{\partial^2 u}{\partial v \partial T} \right) \left(\frac{\partial v}{\partial T} \right)_p + \left(\frac{\partial^2 u}{\partial T^2} \right)_v + p \left(\frac{\partial^2 v}{\partial T^2} \right)_p = 0$ by means of equations (8), (7), (6), (5) and the equation $0 = \left(\frac{\partial^2 p}{\partial v^2} \right)_T$

$\left(\frac{\partial v}{\partial T} \right)_p^2 + \left(\frac{\partial p}{\partial v} \right)_T \left(\frac{\partial^2 v}{\partial T^2} \right)_p + \frac{\partial^2 p}{\partial v \partial T} \left(\frac{\partial v}{\partial T} \right)_p + \left(\frac{\partial^2 p}{\partial T^2} \right)_v$ obtained by differentiating p twice with respect to T and then imposing the condition $p = \text{constant}$.

under these conditions. The entropy could be readily calculated by means of this formula if the continuity temperature function of c_p , which was discussed in the previous Section, were known.

Another formula for the entropy may be obtained on integrating the equation

$$\left(\frac{\partial S}{\partial v}\right)_T = \frac{1}{T} \left\{ \left(\frac{\partial u}{\partial v}\right)_T + p \right\} = \left(\frac{\partial p}{\partial T}\right)_v \quad (46)$$

obtained directly by the help of equation (10), giving

$$S = \int \left(\frac{\partial p}{\partial T}\right) \cdot \partial v + \phi'(T, M_a, M_b, \dots) \quad (47)$$

This equation may be developed along the same lines as equation (19). It can be shown to have the functional form

$$S = \sum M \cdot \psi' \left(T, \frac{M_a}{V}, \frac{M_b}{V}, \dots \right) + \sum M \cdot \phi'(T) \quad (48)$$

Let us suppose that this equation is applied to substances in the gaseous state, which do not undergo appreciable dissociation on varying the volume from v_1 to v_2 . Since no appreciable change in internal energy takes place during this change in volume, the change in entropy of *each* substance is equal to the external work done divided by the temperature, or equal to

$$R \ln v_2/v_1$$

Hence if the entropy of one substance is subtracted from that of another substance, the foregoing term disappears and the resultant difference is independent of v over the range from v_1 to v_2 , and hence independent of the relative masses of the constituents over the same range. It appears therefore that if S_A, S_B, \dots are the entropies of stable substances of the same type in the gaseous state, or rather a set of substances for which the internal energy is additive, the differences $S_B - S_A, S_C - S_A, \dots$ are additive in respect to the atoms they contain. Therefore if the substances contain n different atoms the determination of the entropies of $n + 1$ substances furnishes the value of n differences from which the atomic entropies may be determined. The values of the other differences may then be calculated by means of the additive law. On adding the known entropy S_A corresponding to the volume v to each difference, the entropies of the various substances corresponding to the volume v will be obtained.

This result may be put into the following convenient form: Let $n_1 a_1 + n_2 a_2 + \dots$ denote the formula of a compound of a given type containing n_1 atoms a_1, n_2 atoms a_2 , etc. Let the corresponding formula for the substance whose entropy is S_A be $n'_1 a_1 + n'_2 a_2 + \dots$. The difference between the entropy of one of the substances and the entropy S_A is equal to

$$(n_1 a_1 + n_2 a_2 + \dots) - (n'_1 a_1 + n'_2 a_2 + \dots)$$

where the constants a_1, a_2, \dots have appropriate values. These constants may be determined from the known values of a number of such differences.

The value of the entropy for any one of the substances at the volume v is then given by

$$(n_1 a_1 + n_2 a_2 + \dots) - (n'_1 a_1 + n'_2 a_2 + \dots) + S_A$$

At present there is not sufficient data available to carry out such a set of calculations.

It is of importance to notice that if the values of more entropy differences are known than is necessary to determine the additive constants, the correctness of the additive law may be tested by means of these differences. If an agreement is obtained it is not only evidence of the correctness of the law but also that the values of the entropies used are likely to be correct. A welcome check on the entropy calculations is thus obtained.

Equation (47) may be written

$$S = \int \left(\frac{\partial p}{\partial T} \right)_v \cdot \partial v + \Phi'(T, M_a, M_b, \dots) + \Sigma M \cdot \phi'(T) \quad (49)$$

on comparing it with equation (48), where the function Φ' renders the integral a series of functions of $T, \frac{M_a}{v}, \frac{M_b}{v}, \dots$ each of which has one of the quantities

M_a, M_b, \dots as a factor. The form of this function may be obtained from the equation of state of the substance. If the masses of all the constituents except a are supposed to be zero the equation becomes

$$S_a = \int \left(\frac{\partial p}{\partial T} \right)_v \cdot \partial v + \Phi'(T, M_a, 0, \dots) + M_a \cdot \phi_a'(T) \quad (50)$$

and expresses the entropy of the constituent a at the volume v and temperature T . The functions of the type $\phi'(T)$ may thus be obtained from the equations referring to the elementary substances. We may write, therefore,

$$\Delta S = \Delta \int \left(\frac{\partial p}{\partial T} \right)_v \cdot \partial v + \Delta \Phi'(T, M_a, M_b, \dots) \quad (51)$$

Hence if the equations of state of the complex substance or mixture and of its constituents be known, the entropy of the complex substance may immediately be calculated. The difficulty is that the form of the equation of state that would give the entropy correctly is not known.

It can be shown similarly as in the previous Section that if equation (48) is applied to a complex substance at infinite volume, the expression for the entropy becomes equal to the sum of the entropies of the constituents in the isolated state. Therefore if substances of the same type whose volumes are infinite are mixed no change in entropy takes place.

3. Formulae for the Maximum Work and Free Energy of a Substance or Mixture

The maximum work A is given by

$$A = u - TS \quad (52)$$

At the absolute zero of control $u = 0$ and $S = 0$, and thus

$$A = 0 \quad (53)$$

or the zero of the maximum work is the same as that of the entropy and internal energy. This is not the only point however at which the maximum work is zero, being also zero for values of v and T given by

$$u - TS = 0 \quad (54)$$

This equation represents a curve on a v, T diagram which passes through $v = v_0$ and $T = 0$. On passing from a point on this curve to the axis v the maximum work changes from zero to u since $T = 0$ under these conditions in equation (52), or it becomes a positive quantity. Thus A is a positive quantity corresponding to a given volume for temperatures less than that corresponding to the zero value of A . For higher temperatures the maximum work is negative. At the absolute zero of temperature the maximum work of a substance in any state has the same property as u , namely that the first and second differential coefficients with respect to T at constant volume are zero according to equations (3), (5) and (6).

Various expressions for A may be obtained on substituting in equation (52) the various expressions obtained for u and S in the preceding two sections.

The free energy F is given by

$$F = u - TS + pv \quad (55)$$

Since u, S and p are zero at the absolute zero of control this also holds for F . It is also zero for values of v and T given by

$$u - TS + pv = 0 \quad (56)$$

It can be shown similarly as for the maximum work that for a given volume the free energy is positive at temperatures lower than corresponding to $F = 0$, and negative for higher temperatures. F has the property at the temperature $T = 0$ that the first and second differential coefficients with respect to T at constant volume are zero according to equations (3), (5), (6), (7) and (8).

Various expressions for F are obtained on substituting in equation (55) the expressions obtained for u and S in the preceding two Sections.

An expression for A which is of importance may be obtained on integrating the equation

$$\left(\frac{\partial A}{\partial v}\right)_T = p \quad (57)$$

giving

$$A = \int p \cdot \partial v + \Phi'_1(T, M_a, M_b \dots) \quad (58)$$

This equation may be written

$$A = \int p \cdot \partial v + \Phi'(T, M_a, M_b, \dots) + \Sigma M \cdot \phi'(T) \quad (59)$$

where Φ' is a function which renders the integral a series of functions of T , $\frac{M_a}{v}$, $\frac{M_b}{v}$, ... each of which has one of the quantities M_a, M_b, \dots as a factor.

It can be shown similarly as in the preceding two Sections that the functions $\Sigma M \cdot \phi'(T)$ have the same forms as for the elementary constituents. Hence we may write

$$\Delta A = \Delta \int p \cdot \partial v + \Delta \Phi'(T, M_a, M_b, \dots) \quad (60)$$

The free energy equation corresponding to equation (59) is obtained from equations (54) and (59), thus

$$F = \int p \cdot \partial v + pv + \Phi''(T, M_a, M_b, \dots) + \Sigma M \cdot \phi''(T)$$

$$\text{or} \quad F = \int v \cdot \partial p + \Phi''(T, M_a, M_b, \dots) + \Sigma M \cdot \phi''(T) \quad (61)$$

where Φ'' is a function which renders the integral a series of functions of T , $\frac{M_a}{v}$, $\frac{M_b}{v}$, ... each of which has one of the quantities M_a, M_b, \dots as a factor.

The functions $\Sigma M \cdot \phi''(T)$ correspond to the forms they have for the elementary substances, and hence we may write

$$\Delta F = \Delta \int v \cdot \partial p + \Delta \Phi''(T, M_a, M_b, \dots) \quad (62)$$

Hence if the maximum work and the free energy of the constituents of a mixture and their equations of state and that of the mixture be known, the maximum work and the free energy of the mixture may immediately be calculated by means of equations (60) and (62).

It can be shown similarly as in the preceding two Sections in connection with the internal energy and entropy that we may write

$$A = \Sigma M \cdot \psi''(T, \frac{M_a}{v}, \frac{M_b}{v}, \dots) + \Sigma M \cdot \phi''(T) \quad (63)$$

$$F = \Sigma M \cdot \psi'''(T, \frac{M_a}{v}, \frac{M_b}{v}, \dots) + \Sigma M \cdot \phi'''(T) \quad (64)$$

If we consider a number of complex substances of the same type in the gaseous state which do not appreciably dissociate on changing the volume of each from v_1 to v_2 each of these substances can easily be shown to undergo a change in maximum work equal to $RT \ln v_2/v_1$. Hence if the maximum

work of one of the substances is subtracted from that of each of the other substances the differences should be additive in respect to the atoms. A similar result can be shown to hold for the free energy.

Since the maximum work and free energy are usually calculated from the internal energy and entropy by means of equations (52) and (54), it is most convenient to treat the latter quantities from the additive point of view and calculate their values by the help of the additive law. By direct substitution of these values in equations (52) and (54) the maximum work and free energy of each substance considered is then obtained. The value of the free energy and maximum work of a substance for any other state may then be obtained by means of the equation of state, formula for the heat of evaporation, etc. Thus the foundation is furnished for finding the free energy, the most important quantity to a chemist, for every known chemical compound without the necessity of carrying out specific heat measurements in each case. Within a few years we may therefore see a complete list of values of the free energy of all known compounds for a certain standard state available for the academic and commercial chemist. Knowing the free energy functions of substances their chemical behaviour may immediately be predicted, or the direction in which a chemical change will take place on mixing some of them, and the amount of external work done during the reaction. In particular the corresponding constant of mass-action K_p may be calculated by means of the well known equation¹

$$\Delta F = -RT \ln K_p \quad (65)$$

The additive law dealt with gives some interesting properties of the constant of mass-action in this connection. If we are dealing with the free energies of formation ΔF_a and ΔF_b of two compounds a and b of the same type from the same elemental substances, we may write,

$$\Delta F_a - \Delta F_b = - \{ RT \ln K_{pa} - RT \ln K_{pb} \} = - RT \ln \frac{K_{pa}}{K_{pb}}$$

Now the left hand side of this equation is additive from what has gone before. Hence we will have

$$\left(\frac{K_{pa}}{K_{pb}} \right)^{RT} = A_e^{n_e} A_r^{n_r} \dots \quad (66)$$

where n_e is the difference in the number of atoms e contained in two molecules of the substances a and b with which the constant A_e is associated, n_r the difference in the number of atoms r with which the constant A_r is associated, and so on. These constants are the same for all substances of the same type.

The additive laws developed in this and the preceding two Sections may evidently be used to calculate the entropy, free energy of formation, and the constant of mass action of compounds that have not yet been discovered in

¹ Holds strictly only when the dissociation is small, R. D. Kleeman, Phil. Mag., 5, 263, 1928.

the laboratory. The free energy change may refer to the formation of a compound from the elementary constituents, or from any conceivable substances. Valuable information for actually producing a given compound might in that way be obtained. It might also be pointed out that if some of these atomic additive constants should possess negative values, a method would be afforded of determining the possibility of obtaining any conceivable compound, since its entropy can only have a positive value.

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ADSORPTION AND SOLUTION PHENOMENA ENCOUNTERED IN PRECIPITATIONS*

BY FREDERICK R. BALCAR WITH GEBHARD STEGEMAN**

I. Introduction

In a study of the recovery of ionium from carnotite ore, Kammer and Silverman¹ noted that when barium sulfate is precipitated in solutions of thorium chloride, thorium is removed from the solutions in unusually large quantities, and that the amount removed varies with the concentration of the thorium chloride in a manner that may approximately be described by the Freundlich isotherm.

Inasmuch as the mechanism of adsorption by precipitates is not well known, and since the large amount of adsorption of thorium by barium sulfate might make these substances quite suitable for further study, this investigation was undertaken in the hope that by repetition of the work of Kammer and Silverman, and the study of phenomena allied to the adsorption, information might be obtained that would throw further light on the subject.

II. Experimental Study and Discussion

A. Preparation of Materials.

Thorium chloride of the C. P. grade was purified by precipitating thorium hydroxide from an aqueous solution of the chloride with ammonia. The hydroxide was dissolved in hydrochloric acid, the thorium then precipitated as the oxalate with ammonium oxalate, redissolved in excess, and the solution after filtering was acidified with hydrochloric acid to reprecipitate the oxalate. The oxalate was then dissolved in concentrated sulfuric acid, the solution boiled until white fumes were given off, then diluted with cold water and neutralized with ammonia. Finally the hydroxide was treated with a quantity of hydrochloric acid such that not all the hydroxide was dissolved. The solution was allowed to stand some weeks before final filtering and standardization.

Barium chloride and oxalic acid were purified by several recrystallizations from water.

B. Preliminary Experiments.

1. *The Re-solution of Thorium adsorbed by Barium Sulfate.* As a preliminary experiment it seemed important to attempt a determination of the time required for adsorption by the precipitate to come to equilibrium. To solu-

* An abstract of a thesis presented to the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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¹ Kammer and Silverman: J. Am. Chem. Soc., 47, 2514 (1925).

tions of uniform thorium concentration equal amounts of barium chloride were added and barium sulfate precipitated by the addition of sulfuric acid, with mechanical agitation. The mechanical agitation was continued at constant temperature, 25°C., for different periods of time, and the final concentration then determined. The initial concentration of thorium was 0.2000 grams as thorium oxide in 500 ml. of solution, and the amount of barium sulfate precipitated in each case was 0.9870 grams. The results are shown in Table I.

TABLE I
The Re-solution of Thorium adsorbed by Barium Sulfate

| Time of agitation | 1 hr. | 6 hrs. | 27 hrs. | 3 days | 7 days |
|---------------------|--------|--------|---------|--------|--------|
| Final concentration | 0.1074 | 0.1163 | 0.1232 | 0.1233 | 0.1296 |

It is seen that the concentration of the thorium in the solution increases as the agitation is continued.

2. *The Effect of Thorium Concentration on the Particle Size of Precipitated Barium Sulfate.* Several series of experiments were performed with the view of ascertaining what effect a varied concentration of thorium chloride would have on the particle size of barium sulfate precipitated in the solutions.

Solutions of varied thorium concentration were prepared; equal amounts of barium chloride were added and then precipitated by the addition of equivalent amounts of sulfuric acid. The suspensions were allowed to settle simultaneously in Nessler tubes, and the rates of settling were compared in the various tubes. It was found that as the concentration of thorium increased from zero, the rate of settling at first decreased, going through a minimum at about 0.002 normal concentration, then increased to a maximum and finally decreased until the suspensions did not settle appreciably over a period of days.

No satisfactory explanation can be offered for this peculiar variation of particle size with the concentration of thorium. It may be analogous to the variation of particle size of precipitated barium sulfate observed by P. von Weimarn¹ in the case of varied concentration of the reacting solutions.

The above experiments are sufficient to emphasize the necessity of maintaining uniformity as to time, agitation, and changes in concentration, if the results are to be made comparable.

C. *The Solution of Barium and Lead Sulfates in Thorium Chloride Solutions.*

In the first series of experiments on the adsorption of thorium by barium sulfate, it was found that in the higher concentrations of the thorium, precipitation was incomplete, giving only a slight cloudiness which disappeared entirely on warning.

An attempt to determine the solubility of barium sulfate in thorium chloride solutions was then made in the following manner, without any hope for very great precision. Solutions of varied concentrations of thorium were

¹ Ostwald and Fischer: "Colloid Chemistry", p. 25 (1917).

prepared, and equivalent solutions of barium chloride and sulfuric acid were added alternately drop by drop from burettes while the solution was strongly illuminated by a converging beam of light. As the addition of the reagents was continued and saturation of the solution approached, one drop of each of the reagents gave a Tyndall effect which disappeared in a few seconds. The point at which the Tyndall cone became permanent was taken as the end point representing saturation of the solution. The results are shown in Table II.

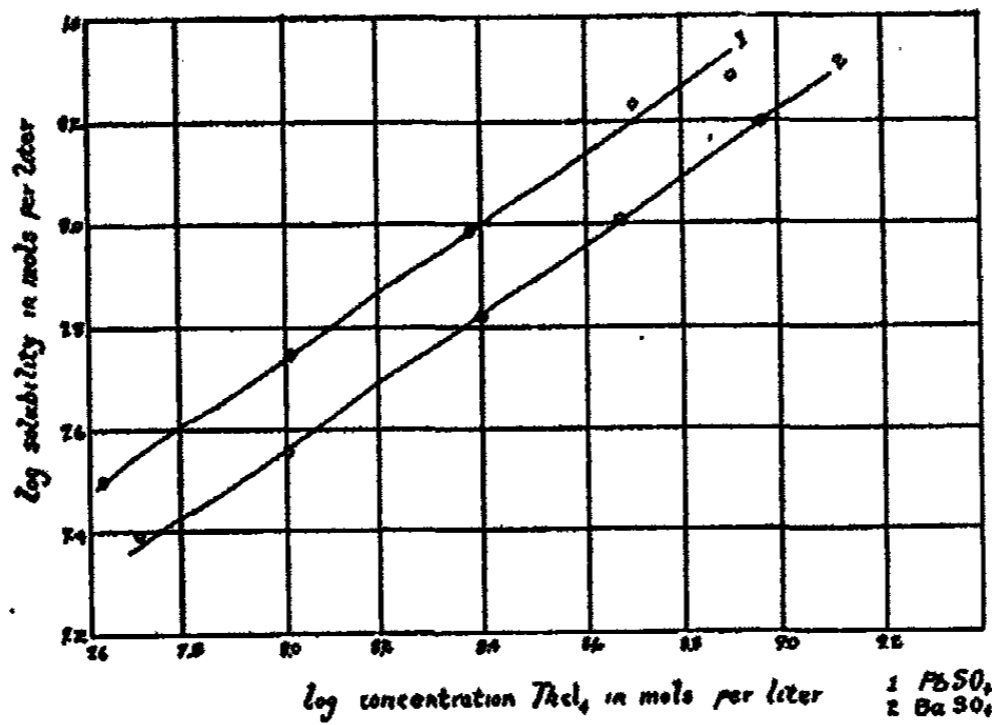


FIG. 1
Solubilities of Lead and Barium Sulfates in Thorium Chloride Solutions.

TABLE II
The Solubility of Barium Sulfate in Thorium Chloride Solutions

| C | S | Log C + 10 | Log S + 10 |
|--------|--------|------------|------------|
| 0.0871 | 0.0153 | 8.9400 | 8.1847 |
| 0.0467 | 0.0103 | 8.6690 | 8.0127 |
| 0.0251 | 0.0066 | 8.4001 | 7.8195 |
| 0.0102 | 0.0035 | 8.0086 | 7.5430 |
| 0.0052 | 0.0025 | 7.7131 | 7.3899 |

C = concentration in mols per liter of ThCl₄.
S = concentration in mols per liter of BaSO₄.

An inspection of the above data shows that when the logarithm of the concentration of barium sulfate is plotted against the logarithm of the concentration of thorium chloride, as in Fig. 1, the points lie near a straight line whose equation is

$$\log S = n \log C + \log K,$$

where *n* and *K* are constants having the values of 0.68 and 0.0789 respectively. The solubility of barium sulfate in thorium chloride may therefore be ex-

pressed by an equation of the same form as the Freundlich isotherm which may be used in describing the variation of adsorption with concentration,

$$S = KC^n,$$

where n and K are the constants empirically determined above.

The same experiment was performed substituting a solution of lead nitrate for the barium chloride. The results, such as they are, appear in Table III, and in Fig. 1, the logarithm of the solubility of lead sulfate being plotted against the logarithm of the concentration of the thorium chloride, along with the data plotted in the case of barium sulfate.

TABLE III

The Solubility of Lead Sulfate in Thorium Chloride Solutions

| C | S | Log C + 10 | Log S + 10 |
|--------|---------|------------|------------|
| 0.0817 | 0.01970 | 8.9124 | 8.2953 |
| 0.0495 | 0.01760 | 8.6946 | 8.2450 |
| 0.0233 | 0.00959 | 8.3711 | 7.9820 |
| 0.0105 | 0.00574 | 8.0233 | 7.7587 |
| 0.0044 | 0.00323 | 7.6499 | 7.5093 |

C = concentration in mols per liter of ThCl_4 .

S = concentration in mols per liter of PbSO_4 .

It is seen that the points in the case of lead sulfate also approximate a straight line, except in the higher concentrations where the end point was uncertain. If the line through the three points representing the lower concentrations be taken as giving the solubility relationship over this range, the line through these points is very nearly parallel to that in the case of barium sulfate. Therefore an equation similar to that used for barium sulfate may be used to describe the solubility of lead sulfate,

$$S' = K'C^n.$$

Not only are the equations of the same form, but as the plotted lines are parallel it follows that the exponent is the same in the two equations, and that the solubilities of the salts over this range are in constant ratio,

$$S/S' = K/K' = 0.642.$$

According to the theory of Debye and Hückel, whose general equations have been simplified by Brönsted and LaMer for the change in solubility of a sparingly soluble salt in solution in a solvent salt, and for the change in the activity coefficient or thermodynamic degree of dissociation of the dissolved salt, the following relations should exist in dilute aqueous solutions,

$$\log f = -\log S/S_0 = 0.5 Z_1 Z_2 \sqrt{\mu}$$

where f is the activity coefficient, S , the solubility of the saturating salt at any concentration of the solvent salt, S_0 , the solubility of the saturating salt in water, Z_1 and Z_2 , the valences of the ions, and μ , the ionic strength of the solution defined as $1/2(C_a Z_a^2 + C_b Z_b^2 + \dots + C_i Z_i^2)$. Obviously the solutions involved in the experiments above are far too concentrated (0.2 to 1.0) to

hope for anything like good agreement with the theoretical solubility of sparingly soluble salts. The values obtained for $-\log S/S_0$ when plotted against the square root of the ionic strength give a line which is slightly concave downwards, whose slope is not far different from the value $0.5 Z_1 Z_2$, but the numerical values of $-\log S/S_0$ are of the order of one hundred times too large. It seems improbable that even in dilute solutions the results would agree with the theory.

This increase in the solubility of sparingly soluble salts has been attributed by many writers to complex ion formation. Dhar and Ghosh¹ summarize evidence which seems to favor this view, and give evidence of their own which leads them to believe that peptization and solution of certain substances are the results of adsorption of the solvent salt by the solid solute, and consequent complex formation.

The formation, however, of clearly defined complexes such as are treated by the older researches on complex ions, seems to be almost out of the question. In the smooth curves here studied there is no hint of definite compound formation with the ratio of barium sulfate to thorium chloride in the solutions varying five-fold.

The fact that barium sulfate and lead sulfate (salts of the same valence type), have different solubilities, seems to indicate that something more than mere stoichiometric ratios must be involved. From the standpoint of activities, the solubilities of these two salts depend on their activity coefficients. According to Lewis and Randall,² the activity coefficient of 0.02 molar $PbCl_2$ is 0.47, and that of $BaCl_2$ at the same concentration is 0.655. The substitution of another anion for the chloride ion should not change the ratio between their activity coefficients, nor should the addition of the same quantity of another electrolyte change this ratio $f_{Pb}/f_{Ba} = 0.72$. Now the inverse ratio of their solubilities in thorium chloride, $S_{Ba}/S_{Pb} = 0.64$, differs by about ten per cent from their activity coefficient ratio. This is at least qualitatively in agreement with what might be expected from the ionic point of view.

D. Equilibrium Conditions in a Solution of Barium Sulfate in Thorium Chloride.

Obviously there must be an equilibrium of some kind between the solute, in whatever state it may exist in the solution, and the barium and sulfate ions.

The following experiment was then performed in the hope of finding a clue that might lead to evidence of a more definite nature: Solutions of equal thorium chloride concentration containing varied amounts of barium chloride were prepared. To these solutions sulfuric acid was added until a precipitate was observed in the beam of light, as in the first experiments on solubility. The results appear in Table IV.

¹ Dhar and Ghosh: *Z. anorg. Chem.*, 152, 405 (1926).

² Lewis and Randall: "Thermodynamics", pp. 362, 423 (1923).

TABLE IV
The Solubility of Barium Sulfate in the presence of Varied Amounts of Barium Chloride

| C_{Ba} | C_{SO_4} | $\sqrt{K_{sp}}$ | S_0/S | $\text{Log } S/S_0 + 10$ |
|----------|------------|-----------------|---------|--------------------------|
| 0.0103 | 0.10033 | 0.01033 | 1.00 | 0.000 |
| 0.0146 | 0.00708 | 0.01020 | 1.46 | 9.834 |
| 0.0201 | 0.00417 | 0.00916 | 2.48 | 9.606 |
| 0.0248 | 0.00232 | 0.00758 | 4.45 | 9.350 |
| 0.0337 | 0.00033 | 0.00320 | 31.00 | 8.570 |

C_{Ba} = concentration in mols/liter of barium chloride.

C_{SO_4} = concentration in mols/liter of sulfuric acid.

K_{sp} = product of the concentration of barium and sulfate ions.

S = the solubility of barium sulfate.

S_0 = the solubility of barium sulfate with no excess of barium present.

Concentration of thorium chloride throughout = 0.05 mols/liter.

It is obvious at once that a relationship as simple as that of the solubility product does not exist, although, it is not to be expected that such a relationship would exist, since the concentrations of the ions are greater than those concentrations in which the solubility product is at best only approximately constant.

If the thermodynamic relations involved in the solubility of a salt in the presence of an excess of one of its ions are valid,¹ then,

$$\sqrt{K_{sp}} \times S_0/S = \text{const.}$$

An inspection of the above data shows that this product is not constant and that the above simple relationship does not exist, although, when the logarithm of S/S_0 is plotted against K_{sp} , as in Fig. 2, p. 1418 the points lie near a straight line whose equation would be of the form

$$\log S/S_0 \times A\sqrt{K_{sp}} + \text{const.}$$

This indicates that there must exist some more complex relationship between solubility and the ion product. If there were involved simply the equilibrium between a complex and its ions, such an equation would not be anticipated. The resemblance which the empirical equation bears to the equations of the interionic theory of the behavior of strong electrolytes might well lead to the suspicion that we deal here with an exaggeration of what Brönsted² terms the specific interaction of ions.

E. The Adsorption of Thorium by Barium Sulfate.

1. *Experimental Procedure.* Following the method of Kammer and Silverman solutions of varied concentrations of thorium chloride were prepared, and varied amounts of barium chloride were added. To these solutions at 25°C., sufficient sulfuric acid was added with mechanical stirring to pre-

¹ Eucken, Jette and La Mer: "Fundamentals of Physical Chemistry", p. 357 (1925).

² Brönsted: J. Am. Chem. Soc., 44, 877 (1922).

precipitate completely the barium as the sulfate. After the addition of the sulfuric acid the suspensions were immediately centrifuged, and aliquot portions of the clear supernatant solution were removed and the residual thorium concentrations determined gravimetrically by precipitation as the oxalate with oxalic acid, and ignition to the oxide. The results are presented in Table V.

TABLE V

| m | Log C ₀ + 10 | Log C + 10 | Log x/m + 10 |
|------|-------------------------|------------|--------------|
| 10.0 | 8.0851 | 7.8115 | 8.8217 |
| 10.0 | 7.8632 | 7.4362 | 8.7267 |
| 5.0 | 8.0851 | 7.9057 | 8.9824 |
| 5.0 | 7.8632 | 7.6071 | 8.8801 |
| 5.0 | 7.6871 | 7.3328 | 8.8014 |
| 3.5 | 7.9881 | 7.7949 | 9.0662 |
| 3.5 | 7.8632 | 7.6293 | 9.0057 |
| 3.5 | 7.6871 | 7.2750 | 8.9198 |
| 2.5 | 7.9881 | 7.8193 | 9.1653 |
| 2.5 | 7.8632 | 7.6645 | 9.0973 |
| 2.5 | 7.6871 | 7.4326 | 9.0030 |
| 2.0 | 8.2008 | 7.9465 | 9.2820 |
| 2.0 | 7.8632 | 7.5900 | 9.1463 |
| 2.0 | 7.6871 | 7.4682 | 9.0508 |
| 1.0 | 7.8632 | 7.7641 | 9.2399 |
| 1.0 | 7.6871 | 7.5690 | 9.1311 |
| 1.0 | 7.3861 | 7.2053 | 8.9850 |
| 0.5 | 7.9881 | 7.9362 | 9.4079 |
| 0.5 | 7.8632 | 7.8030 | 9.3430 |
| 0.5 | 7.6871 | 7.6183 | 9.2209 |
| 0.5 | 7.3861 | 7.2853 | 9.0703 |

m = mass in grams of barium sulfate.

C₀ = initial concentration of thorium chloride in mols per liter.

C = final concentration of thorium chloride in mols per liter.

x/m = mols thorium adsorbed by one mol barium sulfate.

2. *The Variation of x/m with Variation of m.* From the data in Table V it is seen that as m increases x/m decreases. This would indeed be expected since the concentration of thorium decreases as the barium is precipitated. The decrease in x/m, however, is greater than might be accounted for by the change in concentration. When the logarithm of x is plotted against the logarithm of the initial concentration of the barium chloride as shown in Fig. 3, there results a distribution of points which in the lower concentrations of barium chloride is best represented by a straight line through the points. The equation of this line would be

$$\log x = n \log m + \log K,$$

in which n and K are constants, and n has the value of 0.66.

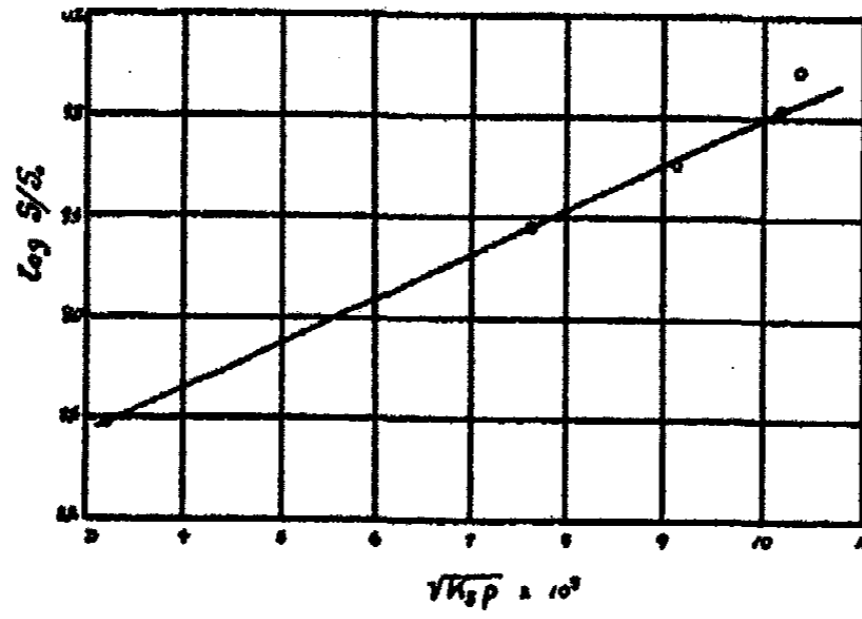


FIG. 2

Equilibrium between Barium and Sulfate Ions in Thorium Chloride Solutions.

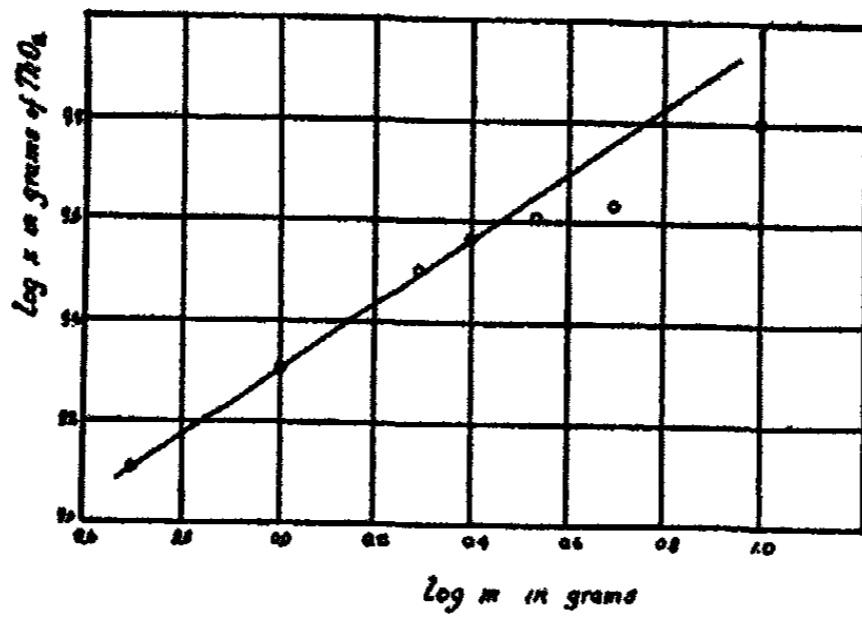


FIG. 3

Variation in the Amount of Thorium Adsorbed.

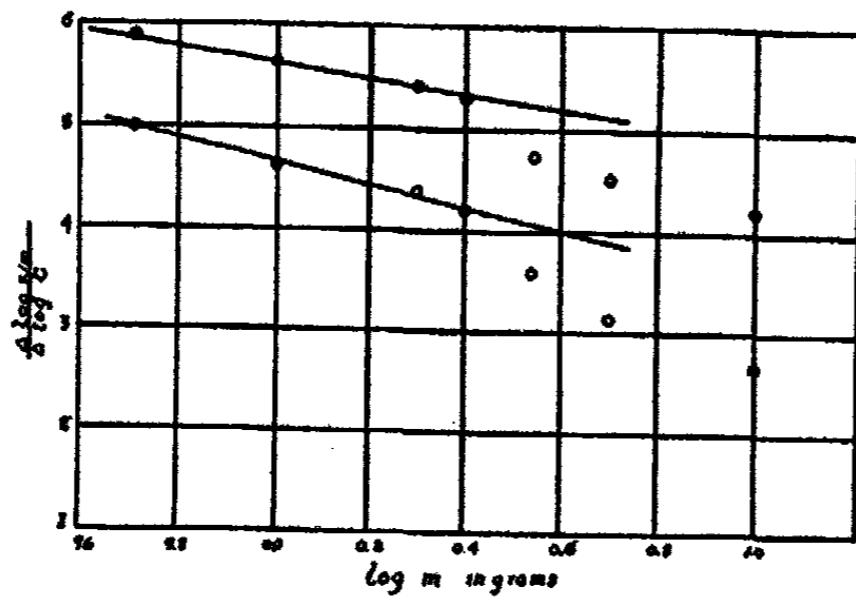


FIG. 4

Variation of the Slopes of the Adsorption Curves.

3. *The Application of Equations to the more general Description of the Adsorption of Thorium by Barium Sulfate.* In Fig. 4 are plotted logarithmically the values of x/m against the final concentration. It is seen that for constant values of m an equation of the form used by Freundlich gives a satisfactory description of the variation of x/m with C over the range of the concentrations studied. If the Freundlich equation applies rigidly, $\log x/m$ plotted against $\log C$ gives a straight line whose slope is $\frac{\Delta \log x/m}{\Delta \log C}$. It is

seen that even in the limited range of concentrations here studied there is a tendency toward a curve which is concave upwards. With the variation

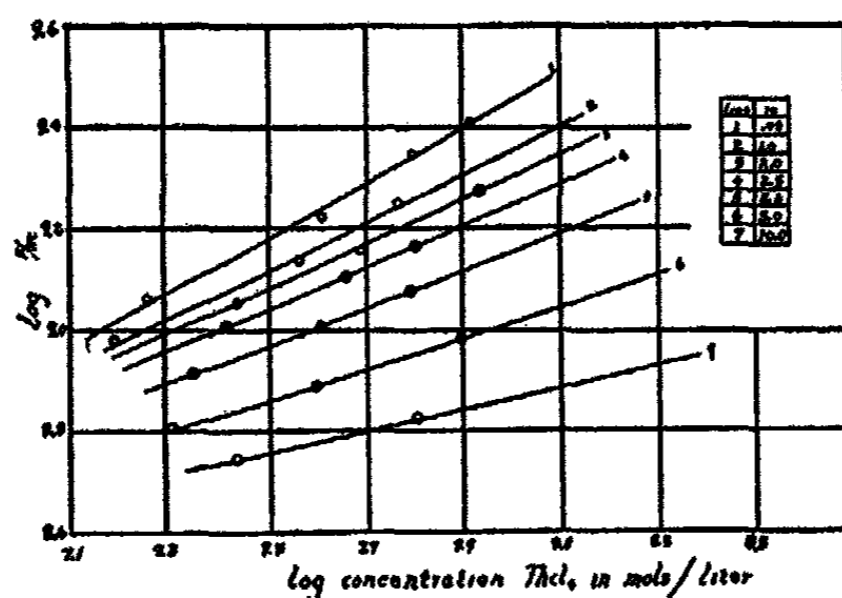


FIG. 5
Adsorption of Thorium on Precipitated Barium Sulfate.

of m , K , which is simply x/m at unit concentration, varies in the manner described above, decreasing as m increases, and as a glance at Fig. 5 reveals, the slope $n = \frac{\Delta \log x/m}{\Delta \log C}$ also decreases as m increases. This variation of n

with m is interesting and perhaps significant.

For the sake of convenience the values of the slopes obtained by plotting logarithmically x/m against C and C_0 , are collected in Table VI.

TABLE VI
The Variation of n with m for C and C_0

| | | | | | | | |
|--------|------|------|------|------|------|------|------|
| m | 0.5 | 1.0 | 2.0 | 2.5 | 3.5 | 5.0 | 10.0 |
| nC_0 | 0.58 | 0.56 | 0.54 | 0.53 | 0.47 | 0.45 | 0.42 |
| nC | 0.50 | 0.46 | 0.44 | 0.42 | 0.36 | 0.32 | 0.26 |

When the values of n are plotted against $\log m$, the points representing the lower values of m lie near straight lines as shown in Fig. 4. It will be noted that the points representing higher values of m fall rather abruptly away from the direction of the straight line. This break in the curve, which is very similar to that observed in the graph in which $\log x$ is plotted against

log m , and which occurs at the same concentration of barium chloride, evidently betrays a difference in the manner of adsorption varying with m , a kind of transition or critical point, on one side of which one equation is valid, on the other side another equation. The equations of the lines are of the form

$$n = \frac{\Delta \log x/m}{\Delta \log C} = A \log m + \log B,$$

in which A and B are constants.

Assuming that the straight line relationships for K and n hold for the smaller values of m , a general equation for the adsorption in this region may be obtained, one that takes into account both the variations of K and n with m .

$$x/m = \frac{KC^F}{\sqrt{m}},$$

in which $F = A \log Bm$.

It is interesting to note that as m decreases, n must approach a limiting value. At the point where so small a quantity of barium sulphate is precipitated that the initial and final concentrations of the thorium chloride are the same, the lines representing the variations of n with m for the initial and final concentrations would intersect. By extending these lines to their point of intersection, it was found that this intersection would occur when the concentration of barium chloride is about 1.5×10^{-4} mols per liter. The corresponding value of n is about 0.66.

The point of zero precipitation is of course the point of saturation of the solution with barium sulfate. An attempt was made to determine this solubility in the manner previously described, using solutions of thorium chloride and sulfuric acid roughly near the average concentrations employed in the solutions studied. This method gave for the solubility a value of about 10^{-4} mols per liter, thus agreeing in order of magnitude with that obtained by the extrapolation of the n curves.

This seems to establish pretty well the limiting value of the slope of the adsorption curves as being in the neighborhood of 0.66. Now this limiting value of the slope of the adsorption curve is so near the value of the slope of the solubility curve of barium sulfate in thorium chloride solutions that it seems to be worthy of note. Evidently with the precipitation of differential amounts of barium sulfate, the adsorption of thorium by barium sulfate varies in somewhat the same manner as the solubility of barium sulfate varies with the concentration of thorium chloride.

III. Summary

A. The resolution of thorium adsorbed by barium sulfate and the effect of thorium chloride on the particle size of barium sulfate precipitated in thorium chloride solutions have been studied.

B. A relation between the concentration of thorium chloride and the solubilities of barium and lead sulfates in solutions of thorium chloride has been found and discussed.

C. The equilibrium between barium and sulfate ions in solutions of thorium chloride has been studied, and an empirical equation deduced which approximately fits the facts.

D. Experiments on the adsorption of thorium on barium sulfate reveal interesting variations in the constants of the adsorption equation.

POTASSIUM FERRO- AND FERRICYANIDES

BY S. H. C. BRIGGS

In a recent paper in this Journal, F. H. Getman¹ has described further experiments on the absorption spectra of the ferrocyanides and ferricyanides of potassium, which are advanced in support of the view that the α - and β -ferrocyanides are identical whereas the α - and β -ferricyanides are isomeric.

Although Getman refers to my first paper on the preparation of the α - and β -ferrocyanides² he appears to have completely overlooked my second paper on the nature of the β -ferrocyanides and the β -ferricyanides³. In this second paper it was shown that potassium β -ferrocyanide consists of crystals of potassium ferrocyanide coloured by an amount of potassium aquopentacyanoferroate $K_2[Fe(CN)_5H_2O]$ too small to be detected by qualitative or quantitative analysis, and that potassium β -ferricyanide is a compound of potassium ferricyanide and potassium aquopentacyanoferrate having the formula $3K_3[Fe(CN)_6], K_2[Fe(CN)_5H_2O]$.

In view of the position in which the subject is left by Getman's paper it appears desirable to draw attention to these conclusions which are in accordance with all the experimental results and were also confirmed by synthesis.

May 21, 1928.

¹ J. Phys. Chem., 32, 187 (1928).

² Briggs: J. Chem. Soc., 99, 1019 (1911).

³ Briggs: J. Chem. Soc., 117, 1026 (1920).

THE ADSORPTION OF HYDROGEN, ETHYLENE, ACETYLENE AND ETHANE BY STANNOUS OXIDE

J. N. PEARCE AND SYLVIA M. GOERGEN

The phenomenon of heterogeneous catalysis has been the subject of numerous investigations. Through the agency of these researches several facts have been established regarding the nature of contact catalysis. The more important of these may be briefly mentioned. (1) A solid cannot catalyze a reaction unless one or more of the reactants are adsorbed on its surface.¹ (2) While the activity of the catalyst and its power to adsorb reacting vapors on its surface do appear to go hand in hand, there is no quantitative relationship between the two phenomena.² (3) Substances which are strongly adsorbed by a catalyst act as "poisons," in that they prevent the reactants reaching the surface of the catalyst. These poisons include foreign substances, —impurities mixed with the reactants. The poison may be one of the products of the reaction; indeed, either of the reactants may act as a poison, if it is so strongly and selectively adsorbed as to prevent contact of the second reactant with the catalyst surface. (4) The activity of the catalyst is markedly influenced by the nature of the heat treatment to which it has been subjected. (5) The maximum catalytic activity does not necessarily occur at the temperature of maximum adsorption; it may only begin where the adsorption is barely measurable. The adsorption capacity may be considered³ as an index of the temperature at which the reaction can be induced. In other words, a lower temperature will initiate a reaction when adsorption is strong.

An extended investigation of the activity of oxide catalysts at temperatures between 300° and 400° by Sabatier and Mailhe⁴ has shown that a majority of the oxides promote two reactions simultaneously, one the process of dehydration, the other, the process of dehydrogenation. The analyses of the gaseous products obtained when the vapor of ethyl alcohol was passed over various oxides at 340° to 350° showed that with certain oxides ethylene only is produced. In general, however, the effluent vapor is a mixture of ethylene and hydrogen in varying proportions, depending on the catalysts used. Thoria behaves almost exclusively as a dehydrating agent under the given conditions; alumina and tungstic oxide are only slightly less active dehydrating catalysts. The oxides of manganese, cadmium, and tin were found to be dehydrogenating catalysts exclusively; their dehydrating power is entirely suppressed. Between the two extremes the dehydrating and de-

¹ Bancroft: *J. Phys. Chem.*, 21, 573, 644, 734 (1917).

² Taylor: Third Report of Committee on Contact Catalysis, *J. Phys. Chem.*, 28, 898 (1924).

³ Pease: *J. Am. Chem. Soc.*, 45, 2296 (1923).

⁴ Sabatier and Mailhe: *Ann. Chim. Phys.*, (8), 20, 341 (1910).

hydrogenating activity of the oxide catalysts vary widely. In general, the greater the dehydrating activity of the oxide, the less is its dehydrogenating activity toward alcohol.

Benton¹ has studied the adsorption of a number of gases by several oxides. In these papers he distinguishes between primary and secondary adsorption, as proposed by Langmuir. According to him, secondary adsorption is exhibited by inert adsorbents, such as charcoal, mica and silica gel, where the tendency of the different liquids to be adsorbed is in the same order as their boiling points, or as their freezing points. Secondary adsorption decreases continuously with rise in temperature, and it does not reach saturation value until a high pressure is attained. Primary adsorption is selective and is due to primary valences. From certain assumptions based on his own data, Benton has devised a method for calculating the relative magnitudes of primary and secondary adsorption. He finds that neither the secondary adsorption nor the total adsorption by oxide catalysts bear any relation to their catalytic activities. The primary adsorption of carbon monoxide is, however, in the same order as the catalytic activity of the oxides.

Bischoff and Adkins² have measured the adsorption of hydrogen, ethylene, and ethane by titanium oxide at 20° and 97°. While the titanium oxides from different sources differed greatly in absolute and relative activities, they showed no similar differences in the adsorption of the gases which were the products of the reactions catalyzed. For a given temperature the volume of gas adsorbed was greatest for ethylene and least for hydrogen. The adsorption of hydrogen and ethylene by zinc oxide and ferric oxide has been studied by Lazier and Adkins.³ Their results indicate that, while there is a qualitative agreement, there is apparently no quantitative relationship between total adsorption and catalytic activity. Rideal⁴ has measured the adsorption of the same two gases by thoria. Taylor and Kistiakowsky⁵ find that at 0° and 100° both zinc oxide and ZnO-Cr₂O₃, per unit weight, have greater adsorption capacities for hydrogen and carbon monoxide than do most metal catalysts. The adsorption of both gases is pronounced at very low pressures and rapidly reaches saturation capacity independent of further increase in pressure.

Thus far, investigations have been limited to oxides which are either wholly dehydrating catalysts, or to those which show both dehydrating and dehydrogenating activity. It seemed advisable, therefore, to continue these studies with an oxide which, according to Sabatier and Mailhe, is a dehydrogenating catalyst only. The present investigation involves the study of the adsorption of hydrogen, acetylene, ethylene and ethane by stannous oxide at 0°, 78.5° and 100°.

¹ Benton: *J. Am. Chem. Soc.*, 45, 887, 900 (1923).

² Bischoff and Adkins: *J. Am. Chem. Soc.*, 47, 807 (1925).

³ Lazier and Adkins: *J. Phys. Chem.*, 30, 353 (1926).

⁴ Rideal: *J. Am. Chem. Soc.*, 49, 116 (1927).

⁵ Taylor and Kistiakowsky: *J. Am. Chem. Soc.*, 49, 2486 (1927).

In a later work, Sabatier¹ states that tin oxide acts catalytically upon ethyl alcohol above 300° as a dehydrating agent. As we might expect at this temperature, the oxide was found to be reduced to the metallic state. The metal itself exhibits marked catalytic activity above its melting point,² but owing to the gradual growth of the large drops of the liquid at the expense of the smaller ones, the active surface of the catalyst is slowly reduced. Brown and Henke³ have also found that tin is an excellent reduction catalyst for nitro-aromatic compounds.

Materials and Apparatus

The tin oxide was prepared by a method similar to that used by Bury and Partington⁴ from an "analyzed" sample of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The label attached guaranteed it to give water-clear solutions and to contain only the following negligible impurities: "Cu, nil; Fe, 0.003; SO_2 , 0.0001; NO_3 , nil." It was therefore used without further purification. 45 grams of the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were first dissolved in 200 cc. of distilled water, clarified by the addition of a minimum amount of constant boiling hydrochloric acid, and then heated in contact with metallic tin. This solution was then slowly added, with rapid stirring, to a solution containing an amount of Na_2CO_3 just sufficient to neutralize the free acid and to precipitate the tin as $\text{Sn}(\text{OH})_2$. The precipitate was repeatedly washed by decantation until it no longer settled on standing. It was then filtered on a Büchner funnel, washed, dried at room temperature, and finally stored in a vacuum desiccator over solid KOH. Bury and Partington report that stannous hydroxide reacts with air only slightly, if at all. They state that their dried product corresponds to the formula: $3\text{SnO} \cdot 2\text{H}_2\text{O}$.

The technique employed in this work differs from that of Bury and Partington in that they reversed the procedure and added the Na_2CO_3 solution to that of the tin chloride. When we followed their method we found that the reaction product was frequently contaminated by traces of SnCl_2 . Further, the product exhibits a considerable tendency to turn gray, and even black during the process of decantation, especially if the walls of the vessel are scratched. Using our procedure, the product is always white. When heated in air the oxide readily takes fire and becomes incandescent during the oxidation.

The dried stannous oxide thus prepared was ground to pass through an 100-mesh sieve, and then heated in an atmosphere of CO_2 at the temperature of boiling aniline until the evolution of moisture ceased. The final product was yellow.

The hydrogen used was prepared by electrolyzing a concentrated solution of KOH between nickel electrodes. The gas was then passed through an

¹ Sabatier: "Catalyse", 100 (1927). Translation by Dr. B. Finkelstein.

² Rideal and Taylor: "Catalysis in Theory and Practice", 214 (1919).

³ Brown and Henke: J. Phys. Chem., 27, 739 (1923).

⁴ Bury and Partington: J. Chem. Soc., 121, 1998 (1922).

alkaline solution of pyrogallol, concentrated H_2SO_4 , and finally through a tube containing P_2O_5 .

The commercial ethylene showed by repeated analysis a 99.7 percent absorption in fuming H_2SO_4 . It was passed over fused $CaCl_2$ and then through a trap immersed in a freezing mixture of solid CO_2 and ether.

The ethane was made by the Grignard method.¹ It was further purified by passing it successively through alcoholic $AgNO_3$ and concentrated H_2SO_4 .

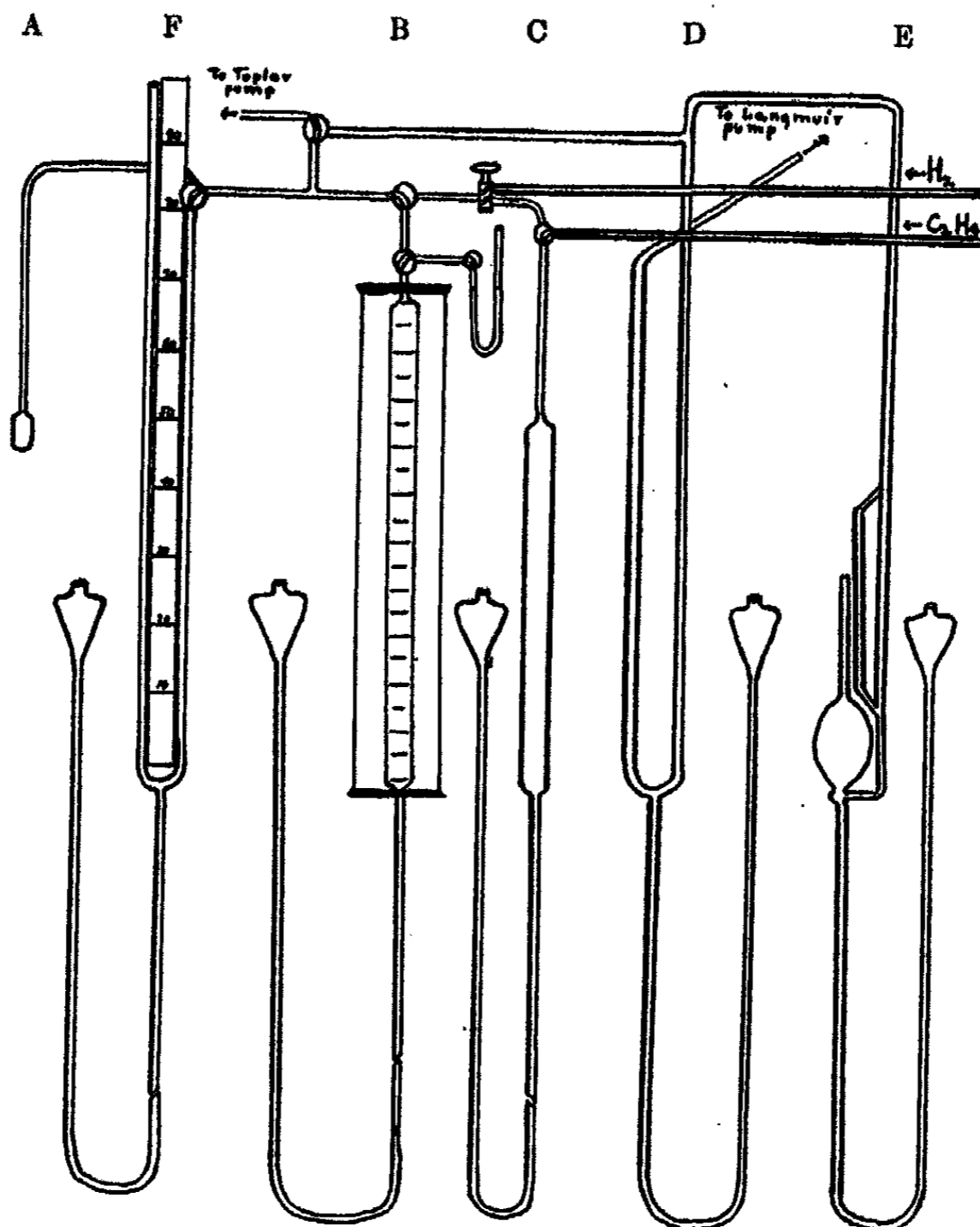


FIG. 1

Acetylene prepared from calcium carbide and water was first allowed to stand over water to remove the soluble impurities and then further purified by passing it successively through a 40 percent solution of KOH , a 1 N solution of $CuSO_4$, concentrated H_2SO_4 , and over P_2O_5 .

The nitrogen was made from equivalent quantities of NH_4Cl and $NaNO_3$. It was dried by passing through concentrated sulphuric acid and phosphorus pentoxide.

¹ Grignard and Tissier: *Comptes rend.*, 132, 835 (1901).

The helium used in determining the dead space was purified by passing it through a liquid air trap containing an activated charcoal which had been evacuated previously at red heat.

The apparatus, Fig. 1, is very similar to that used by Pease.¹ The bulb A containing the tin oxide is connected with the apparatus by capillary tubing. The manometer F, provided with a meter stick, is used to measure the pressure in the bulb A. The accurately calibrated burette B is surrounded by a water jacket containing a completely immersed standard thermometer. To it is attached a small manometer which permits accurate adjustment of the pressure within the burette. The large tube C is a gas reservoir for storing pure gases or their mixtures. The U-tube D serves as a valve for eliminating the pumps, and E is the McLeod gauge. Mercury is used as the displacing liquid throughout the apparatus.

Experimental Procedure

The entire apparatus is evacuated by means of a mercury vapor condensation pump in series with a "Hyvac" oil pump until the McLeod gauge indicates a pressure of less than 0.001 mm. The evacuation of the bulb is made difficult because of the tendency of the oxide to "puff" over. To avoid this completely the oxide bulb is first cautiously opened to the previously evacuated manometer F. By allowing the mercury to drop slowly in F the gases in A are gradually removed. During this evacuation the bulb A is surrounded by the vapor of boiling aniline. When the pressure of the gases has been reduced to a few mms. the bulb is then opened directly to the pumps and is evacuated with the remainder of the apparatus. When the pressure as indicated by the McLeod gauge is sufficiently low and constant the well at D is raised and the stopcock is closed. The pure gas to be studied is then introduced into B and carefully adjusted to atmospheric pressure. In the meantime, the bulb A has been immersed in a Dewar flask containing ice and water, or in the vapor of a boiling liquid, depending on the temperature desired. When thermal equilibrium has been attained a small amount of gas is admitted from B and its equilibrium pressure is determined. This procedure is repeated until the pressure within the bulb is approximately that of the atmosphere. From 7 to 9 additions of gas are made at each temperature. All gas volumes are corrected to 0° and 760 mm.

The "dead space" was determined in the usual way by means of helium. To this end we carefully determined and plotted the pressure-volume isotherms of helium and the several gases at 0°, 78.5° and 100°. These graphs were readable to ± 0.01 cc. The values used in making our calculations were read from these P-V isotherms at even pressures. If we assume that the helium is not adsorbed by the oxide, then the difference between the number of cc. of helium and that of any other gas necessary to produce the same pressure at the given temperature gives directly the volume of the gas adsorbed. Since we did not use exactly 10 g. of oxide, these volumes were recalculated to give the volumes adsorbed by 10 g. at even pressures. The data thus accumulated are given in Tables I-V.

¹ Pease: J. Am. Chem. Soc., 45, 1195 (1923).

TABLE I
Volumes of Various Gases adsorbed by 10 Grams of Stannous Oxide at 0°.
(Sample I).

| P. cm. | H ₂ cc. | C ₂ H ₄ cc. | C ₂ H ₆ cc. |
|-----------|-----------------------|--------------------------------------|--------------------------------------|
| 5 | 0.06 | 0.29 | 0.70 |
| 10 | 0.06 | 0.59 | 1.38 |
| 20 | 0.07 | 1.16 | 2.51 |
| 30 | 0.12 | 1.73 | 3.50 |
| 40 | 0.18 | 2.27 | 4.50 |
| 50 | 0.20 | 2.74 | 5.37 |
| 60 | 0.22 | 3.19 | 6.21 |
| 70 | 0.25 | 3.64 | 7.04 |
| 75 | 0.26 | 3.84 | |

TABLE II
Volumes of Hydrogen and Ethylene adsorbed by 10 Grams of Oxide at 100°.
(Sample I).

| P. cm. | H ₂ cc. | C ₂ H ₄ cc. |
|-----------|-----------------------|--------------------------------------|
| 5 | 0.05 | 0.18 |
| 10 | 0.11 | 0.34 |
| 20 | 0.16 | 0.74 |
| 30 | 0.20 | 1.10 |
| 40 | 0.25 | 1.50 |
| 50 | 0.26 | 1.91 |
| 60 | 0.25 | 2.29 |
| 70 | 0.25 | 2.67 |
| 75 | 0.25 | 2.82 |

TABLE III
Volumes of Various Gases adsorbed by 10 Grams of Stannous Oxide at 0°.
(Sample II).

| P. cm. | H ₂ cc. | C ₂ H ₂ cc. | C ₂ H ₄ cc. | C ₂ H ₆ cc. |
|-----------|-----------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| 5 | 0.03 | 0.86 | 0.71 | 0.86 |
| 10 | 0.06 | 1.49 | 1.31 | 1.61 |
| 20 | 0.09 | 2.75 | 2.46 | 3.02 |
| 30 | 0.10 | 3.93 | 3.47 | 4.23 |
| 40 | 0.13 | 4.99 | 4.42 | 5.33 |
| 50 | 0.18 | 6.02 | 5.27 | 6.45 |
| 60 | 0.21 | 7.00 | 6.14 | 7.48 |
| 70 | 0.24 | 7.84 | 6.87 | 8.53 |
| 75 | 0.27 | 8.27 | 7.20 | |

TABLE IV
 Volumes of Various Gases adsorbed by 10 Grams of Stannous Oxide at 78.5°.
 (Sample II).

| P. cm. | H ₂ cc. | C ₂ H ₂ cc. | C ₂ H ₄ cc. | C ₂ H ₆ cc. |
|-----------|-----------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| 5 | 0.06 | 0.20 | 0.14 | 0.21 |
| 10 | 0.09 | 0.42 | 0.29 | 0.41 |
| 20 | 0.18 | 0.73 | 0.52 | 0.70 |
| 30 | 0.26 | 1.08 | 0.74 | 0.96 |
| 40 | 0.27 | 1.41 | 0.97 | 1.21 |
| 50 | 0.29 | 1.74 | 1.18 | 1.47 |
| 60 | 0.28 | 2.05 | 1.39 | 1.69 |
| 70 | 0.26 | 2.38 | 1.63 | 1.96 |
| 75 | 0.27 | 2.54 | 1.76 | 2.13 |

TABLE V
 Volumes of Various Gases adsorbed by 10 Grams of Stannous Oxide at 100°.
 (Sample II).

| P. cm. | H ₂ cc. | C ₂ H ₄ cc. | C ₂ H ₆ cc. |
|-----------|-----------------------|--------------------------------------|--------------------------------------|
| 5 | 0.04 | 0.10 | 0.10 |
| 10 | 0.07 | 0.20 | 0.19 |
| 20 | 0.11 | 0.38 | 0.36 |
| 30 | 0.17 | 0.57 | 0.54 |
| 40 | 0.20 | 0.69 | 0.70 |
| 50 | 0.22 | 0.84 | 0.90 |
| 60 | 0.27 | 0.96 | 1.07 |
| 70 | 0.26 | 1.06 | 1.25 |
| 75 | 0.28 | 1.12 | 1.36 |

Duplicate series of adsorption measurements were made for each gas at a given temperature, and the P-V isotherms were carefully plotted. In general, the points obtained for the two series were found to lie almost exactly on the same smooth curve. When the two curves did not coincide, the adsorption measurements were repeated. On the whole, the adsorption data for the different gases are easily reproducible at these temperatures.

The relative adsorption magnitudes are most clearly indicated by Figs. 2 and 3, representing adsorption on samples I and II, respectively. Because of the fact that the adsorption of hydrogen by both samples is so small and so nearly identical at all temperatures, only one curve for hydrogen has been plotted. The adsorption of the other three gases is large, and especially so at 0°. With rise in temperature the magnitude of the adsorption decreases rapidly. The effect of rise in temperature upon the volume of the hydrocarbons adsorbed at any pressure is greatest for ethane and least for ethylene. At the higher temperatures the isotherms flatten and become almost rectilinear

at the higher pressures. At 0° ethane is the most highly adsorbed. With this exception the magnitude of the adsorption decreases at all temperatures in the order: C_2H_2 , C_2H_6 , C_2H_4 , H_2 .

No isotherm could be obtained for acetylene at 100° . When acetylene was admitted to the catalyst bulb it showed no tendency to attain an equilibrium pressure, even over a period of six days. From the time that the gas was admitted the pressure began to drop slowly and at a continuously decreasing rate. The acetylene must, therefore, either decompose into carbon and hydrogen, and the hydrogen then react with the oxide, or it must undergo polymerization. The adsorption isotherm for hydrogen at 100° was then

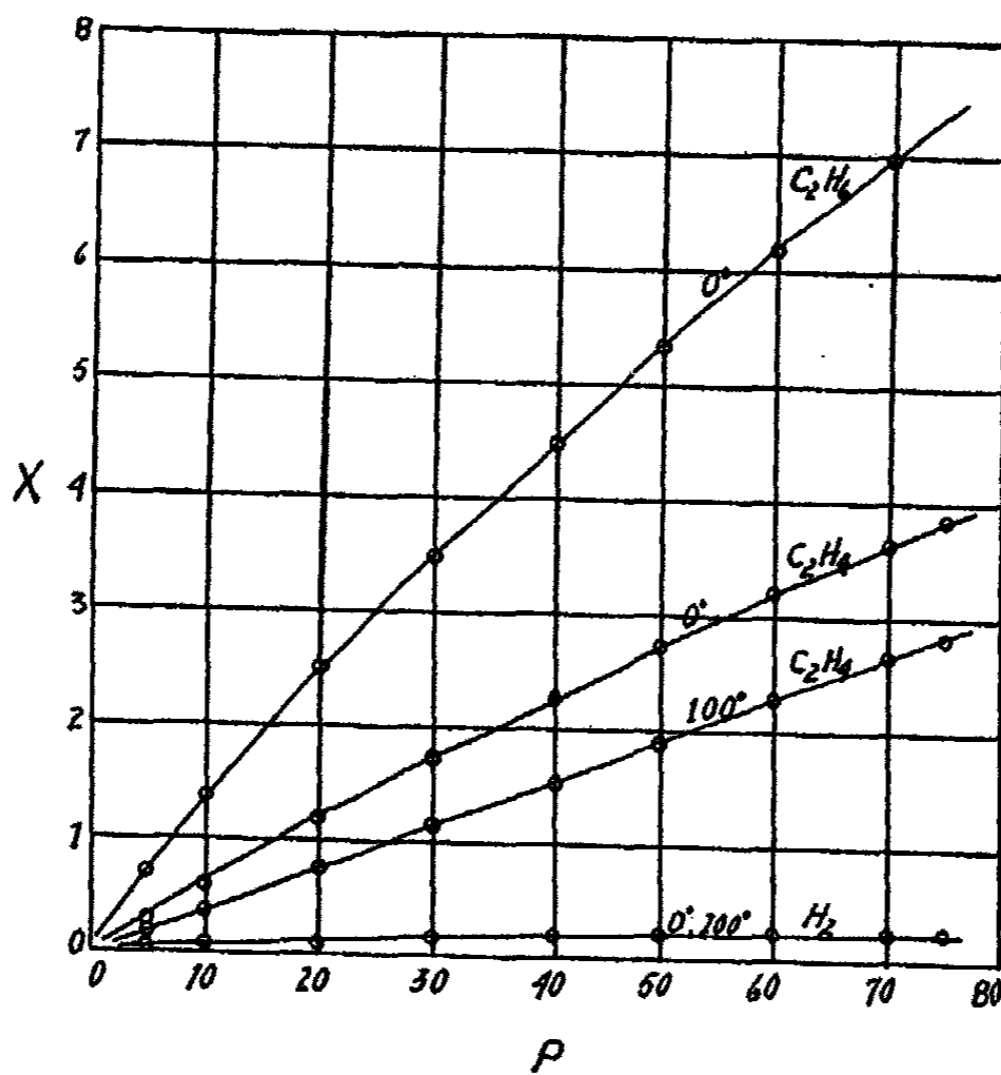


FIG. 2
Adsorption Isotherms at 0° and 100° . Sample I.

carefully determined. As may be seen in Fig. 3, there is no distinct evidence of any reaction between the oxide and hydrogen at this temperature. This, then, eliminates the possibility of the formation of water vapor and the subsequent decrease in pressure due to its adsorption or condensation. If free hydrogen were formed by the decomposition of the acetylene and it remained as a gas, the pressure in the oxide bulb should increase with time, since it is less adsorbed than the acetylene from which it would be formed. If, again, the hydrogen which might thus be formed were to reduce other acetylene molecules to ethylene, or possibly to ethane, the pressure should decrease as the reduction proceeds. In either case amorphous carbon should be formed and its presence would be indicated by a darkening of the oxide surface. No

such discoloration was observed. We must conclude, therefore, that acetylene is polymerized slowly by stannous oxide at 100°.

In a study of the effect of a large number of catalysts upon the reactions of ethylene, Walker¹ has found that acetylene in glass is stable toward heat at temperatures up to 450°. Above this temperature acetylene is polymerized to a brown fluorescent liquid; it decomposes also to a slight extent into carbon, hydrogen and methane and some ethylene is formed by hydrogenation.

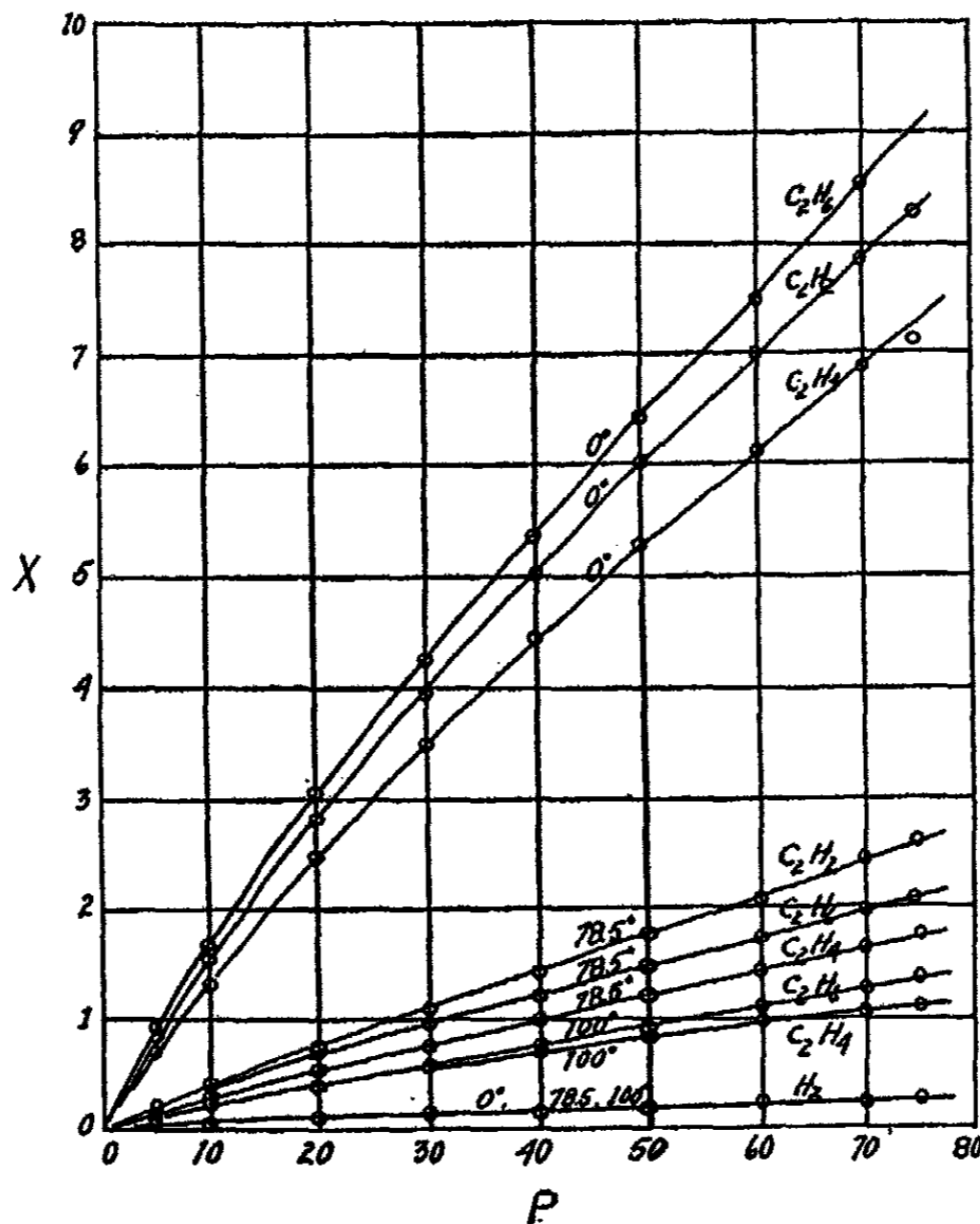


FIG. 3
Adsorption Isotherms at 0°, 78.5° and 100°. Sample II.

Likewise, under similar conditions, he found that a temperature of 650° is necessary to polymerize and decompose ethylene.

For reasons to be mentioned later two samples of the stannous oxide were used. With sample I the isotherms were determined for C₂H₄, H₂ and C₂H₂ at 0°, and for H₂ and C₂H₄ at 100°. With either sample it was found possible to use the oxide first with one gas, then with a second, and finally back to the first without showing any impairment in adsorptive properties, so long as the oxide was not reduced. Both samples were prepared up to the Sn(OH)₂

¹ Walker: J. Phys. Chem., 31, 961 (1927).

stage at the same time. Sample I was taken immediately after formation and subjected to heating and evacuation. Sample II was allowed to stand in a vacuum desiccator over solid potassium hydroxide for about six months, during which it acquired a light yellow surface film. It was subjected to the same heat treatment as sample I before using. Both samples became yellow throughout in the final heat treatment. While the order of the adsorption isotherms for the various gases is the same for both samples, the actual values for any particular pressure differ markedly. The adsorption by sample I is less than that by sample II at 0° ; exactly the reverse is true at 100° , the adsorption by II being less than that by I. It is evident, therefore, that the rate of dehydration of the hydroxide does exert a marked influence on the surface properties of the oxide.

The possibility that stannous oxide might catalyze the hydrogenation of ethylene led us to attempt to determine the velocity of the hydrogenation process. A mixture containing equal volumes of hydrogen and ethylene was introduced into the adsorption bulb at 0° and the pressure readings were taken at frequent intervals. The very slight decrease in pressure within the bulb over a 24 hour interval was so small that the reaction, if any, was inappreciable. A second experiment at 0° verified this conclusion. Duplicate experiments with similar 50 percent volume mixtures were repeated at 100° . Here also no measurable reaction was detected.

Because of the relatively great difference in the adsorption of hydrogen and ethylene, it seemed advisable to increase the proportion of hydrogen in the reaction mixture. Hence, a mixture containing 70.5 percent by volume of hydrogen was made up in the gas burette and accurately checked by analysis. When this mixture was introduced into the catalyst bulb at 0° , the final equilibrium pressure after thirty-two hours was only 0.8 cm. lower than it would have been, assuming that no reaction had taken place. Another portion of the same mixture was then introduced into the previously evacuated bulb at 100° and the change in pressure was observed over a period of twelve days. During this period the total decrease in pressure amounted to 11 cm.; even then there was no indication of the attainment of a constant equilibrium pressure. The free gas was pumped off and its ethylene content was determined in the usual way by absorption in fuming sulphuric acid. Analysis showed 23.9 percent C_2H_4 , as compared with 29.5 percent in the original mixture. To be sure, the change in the percentage of ethylene was not entirely due to chemical reaction, but was due in part to a small amount of adsorbed ethylene which was not removed by complete evacuation. The fraction of ethylene remaining adsorbed under these conditions at 100° would be too small to account for the total decrease in the proportion of ethylene. This, and the continued drop in pressure within the bulb leaves little doubt that a very slow reaction was taking place.

Knowing that a rise in temperature should increase the reaction velocity, we submitted another sample of the (70.5-29.5) mixture to a temperature of 183° . Again the pressure continued to drop, but this time more rapidly. After contact with the oxide for 15 hours the mixture was pumped

out and analyzed. This time the analysis showed 41.4 percent of C_2H_4 ,—an increase in the proportion of ethylene. This behavior indicated that the hydrogen must be reacting with the stannous oxide. To verify this supposition hydrogen alone was admitted to the bulb at 0° and the equilibrium pressure was read. The temperature was then raised to 100° and again a definite equilibrium pressure was obtained. Finally, the bulb was heated to 183° . At this temperature no equilibrium was attained: the pressure within the bulb continued to drop over a period of 12 hours. The bulb was then cooled to 0° , and the pressure was found to be 37.85 cm., whereas the initial pressure at 0° was 47.26 cm. This decrease in pressure indicates conclusively that stannous oxide is reduced by hydrogen at temperatures as low as 183° .

Since the composition of the oxide was unquestionably changed by the reduction, the material was rejected and the adsorption experiments were continued on sample II. This accounts for the apparent incompleteness of the adsorption data for sample I.

The surprisingly low reduction temperature of stannous oxide brought the study of the hydrogenation velocity to a sudden end. The experimental results do show, however, that stannous oxide does slowly catalyze the reaction at 100° , when the mixture of hydrogen and ethylene is approximately 3 to 1. A 50 percent mixture gives no detectable reaction velocity. This is not surprising when we consider the relatively high adsorption of the ethylene at 100° . As the mixture becomes richer in hydrogen the possibility of its being adsorbed even in the presence of the more readily adsorbed ethylene is increased. From the results obtained it would also appear that the simultaneous adsorption of both hydrogen and ethylene is necessary before hydrogenation can take place. However, the ethylene may be adsorbed so highly that it will inhibit the adsorption of the hydrogen to an appreciable extent.

Summary

The adsorption isotherms of H_2 , C_2H_2 , C_2H_4 and C_2H_6 upon stannous oxide have been determined at 0° , 78.5° and 100° .

The adsorption of hydrogen is very small at all temperatures. The adsorption of the three hydrocarbons is relatively large and decreases rapidly with rise in temperature.

Hydrogen reduces stannous oxide at temperatures as low as 183° . The acetylene is polymerized slowly in contact with the oxide at 100° .

Hydrogenation can take place at 100° only when the proportion of the hydrogen in the mixture is relatively very large. This would indicate that the adsorption of hydrogen is necessary before the reaction can take place.

*Physical Chemistry Laboratory,
State University of Iowa.
May 5, 1928.*

NEW BOOKS

Organic Chemistry for Advanced Students. *Julius B. Cohen. Vols. I, II, III. Fifth edition. 21 × 15 cm; pp. vii + 428; pp. vii + 487; pp. vii + 440. New York: Longmans, Green and Co.; London: Edward Arnold and Co., 1928. Price: \$6.00 per volume.* In the preface, p. iii, the author says: "The last decade has seen an unusual development of organic chemistry, more especially in this country, where the additional facilities and inducements for post-graduate research, afforded by grants and research scholarships from public funds, has resulted in a bewildering accumulation of new facts and new ideas. It follows that the student desirous of making himself familiar with the more important advances in the subject may waste much of his valuable time in trying to winnow the chaff from the grain.

"The object of the present edition is to bring the various topics up to date whilst retaining an account of their early history. By condensing some of the less important sections, and by eliminating other portions, which have been superseded by subsequent research, the size of the present edition is only slightly larger than the last."

The first volume is devoted to reactions and the chapters are entitled: historical introduction; valency of carbon; nature of organic reactions; dynamics of organic reactions; abnormal reactions.

The author speaks, very properly, of radicals, and says, p. 1, that "it is an interesting and curious fact that, with admittedly 'little to recommend it', the Chemical Society of Great Britain has seen fit to alter the original spelling to 'radicle,' and the Society now holds the unique position of being the only representative body of chemists which has adopted this spelling." It must be said, however, that the Chemical Society no longer insists that esters shall be called ethereal salts.

"Gomberg and his co-workers have shown by comparing careful molecular weight determinations of various triarylmethyls that with changes of temperature and of dilution in various solvents change of colour does not run parallel with dissociation and that consequently the colour change must be attributed to tautomerism between a benzenoid and quinoid form," p. 63.

"A number of recent observations appear to indicate that nitrogen may exist in a quadrivalent form. The formation of a deep blue colour has been noticed when alkyl or acyl pyridyls are reduced. These blue solutions on absorbing oxygen are decolourised and it was consequently assumed that the blue colour was due to compounds containing bivalent nitrogen. Further investigation has however made it clear that the substances are dipyrindyl derivatives, though there is a difference on the part of different observers in the interpretation of the facts. Dimroth regards these compounds as possessing the structure of a quinhydrone, consisting of two dipyrindyl groups. Weitz, on the other hand regards them as monomolecular dipyrindyl compounds. Emmert inclines to the quinoid formula.

"When a solution of a tetralkylammonium iodide in liquid ammonia is electrolysed or when the chloride is acted on by metallic potassium, a blue solution is formed which reacts in many respects like a solution of the alkali metals in the same solvent. For example, it gives a characteristic deep yellow with dimethylpyrone which is scarcely distinguishable from dimethyl pyrone potassium. Schlubach regards the blue compound as the free ammonium radical; which therefore contains quadrivalent nitrogen," p. 66.

"There are a number of compounds in which there is reason to believe that bivalent carbon is present. Among these are carbon monoxide, CO; fulminic acid, C:NOH; and, according to Nef, the alkyl and acyl isocyanides, RN:C, and acetylene and its halogen derivatives. Although it is possible to interpret the structure of all these compounds, except the last, as containing mutually saturated valencies by making oxygen quadrivalent or nitrogen quinquivalent, there are chemical as well as stereochemical considerations which

make such a supposition improbable. If we accept the usual stereochemical arrangement of the carbon bonds, it is difficult to conceive of these four linkages being brought simultaneously into action with any other single atom. The chemical properties of most of these compounds point in the same direction," p. 68.

"By an unsaturated group, as distinguished from an unsaturated atom, we wish to imply the union of two atoms whose affinities are not saturated. When the union lies between carbon and carbon we obtain the unsaturated hydrocarbons and their derivatives. It is clear that in a case of this character, as, for example, in ethylene and acetylene, we may indicate unsaturation in several ways. Adopting Werner's view that valency may distribute itself unequally over the atom, a larger amount will be available for uniting unsaturated than for saturated carbon, or unsaturation may be indicated by the union of bivalent or trivalent carbon atoms, leaving a certain amount of affinity free, or, again, the unsaturated valencies may be represented by the method adopted by Nef in bivalent carbon compounds, as saturating one another. In the last case we obtain what are known as double or treble bonds or linkages. Although the double and treble bond is very generally accepted, it may be well to state briefly the evidence upon which it rests. We will then proceed to discuss the theory of free valencies, i.e. the union of bivalent and trivalent carbon, and finally Werner's theory in its application to unsaturated compounds," p. 77.

"The union of ethylene and bromine is almost inhibited in a vessel coated with paraffin wax, whereas a glass surface allows the reaction to proceed, and is further accelerated by a stearic acid film. The effect is ascribed to the presence in the latter cases of a polar catalyst," p. 126.

"A more comprehensive theory of catalysis which has found many supporters is that of Langmuir. Based on numerous experiments on gases with tungsten wire in high vacua and also with platinum and palladium, Langmuir concludes that the metal surface is capable of holding a film of substance one molecule thick to which it adheres more or less firmly. Reaction may then take place (1) between molecules or atoms adsorbed in adjacent spaces, (2) between the adsorbed films and the underlying solid, and (3) between the adsorbed film and the colliding gas molecules. Thus the interaction of oxygen and hydrogen in presence of platinum is attributed to the adjacent adsorbed atoms, whilst between carbon monoxide and oxygen it is between oxygen atoms and the colliding carbon monoxide molecules. If the film under the conditions of the experiment is not readily removed from the metal surface the reaction stops. The film acts as a catalyst poison," p. 180.

"With palladium and hydrogen ethylidene malonic ester gives ethyl malonic ester; but with sodium amalgam effects a union of the molecules by linking up the β carbon atoms," p. 183.

"Condensation may then be defined as the union of two or more organic molecules or parts of the same molecule (with or without elimination of component elements) in which the new combination is effected between carbon atoms," p. 195.

"The work of Zincke and Hantzsch on the action of chlorine in alkaline solution on the phenols and other aromatic compounds has afforded numerous examples of the change of a 6-carbon ring into a 5-carbon ring. We may take the case of ordinary phenol which passes into a derivative of cyclopentane. Most of the other phenols behave in a similar fashion. Wreden found that when benzene is reduced with hydriodic acid at 300°, it yields a hydrocarbon C_6H_{12} , which was at first mistaken for cyclohexane; but its low boiling-point (70°) and its conversion into a mixture of glutaric, succinic, and acetic acids on oxidation left no doubt as to its identity with methylcyclopentane. Zelinsky also found that cyclohexanol, on reduction with hydriodic acid, gives a mixture of cyclohexane and methylcyclopentane. Aschan has since shown that cyclohexane changes to methylcyclopentane on simply heating in a closed tube with or without aluminium chloride," p. 209.

The activity concept is apparently working its insidious way into organic chemistry, p. 320. "More recently the question of the significance which should be attached to the term 'active mass' has been much discussed. In the case of gaseous reactions at moderately

low pressures, the volume concentration would seem to afford a satisfactory measure of this quantity. The matter is much less simple when the reacting substances are present in large concentrations in a liquid medium. In such cases the active mass is, in all probability, more appropriately measured by the 'activity' or thermodynamic concentration, the value of which may be obtained from measurements of vapour pressure or from osmotic data, and in the case of ionized reactants from measurements of potential difference."

It was rather interesting to read, p. 378, that "although empirical in origin, the Arrhenius formula has been given a theoretical basis in terms of the so-called radiation theory of chemical change."

"It must be confessed that we are still profoundly ignorant of the change which substituents effect in the character of the molecule as a whole, the causes which determine the rules of orientation, the reason why positive groups like methyl and amino groups facilitate nitration, sulphonation, acetylation by the Friedel-Crafts method, etc., why negative groups assist hydrolysis of cyanides, reduction of nitro groups, acetal formations, etc., and a host of other phenomena of a similar nature. Until clearer views obtain on these subjects it can scarcely be hoped that real progress will be made on the nature of chemical change. The expression 'steric hindrance' meantime affords a useful if not a very appropriate title for docketing a number of allied phenomena," p. 411.

The second volume deals with structure and the chapters are entitled: physical properties and structure; colour and structure; isomerism and stereoisomerism; stereochemistry of unsaturated and cyclic compounds; stereochemistry of nitrogen; isomeric change; the benzene theory.

"Violuric acid and its dimethyl and diphenyl derivatives, together with some of their esters, are colourless or faintly coloured, but yield brightly-coloured salts. Not only do different metals and organic bases produce differently coloured salts; but the same metal yields differently coloured salts and solutions according to the solvent employed. The phenomenon of one salt existing in differently coloured varieties is termed by Hantzsch *pantochromism*. Potassium, rubidium, and caesium diphenyl violurate can each exist in blue and red modifications, and lithium diphenyl violurate gives both red and yellow salts," p. 118.

The author trusts Ostwald and not his own knowledge of organic chemistry, when he says, p. 137, that "methyl orange, on the other hand, is a moderately strong acid whose ion is yellow, whereas the non-ionized molecule is red." Actually, methyl orange as an indicator is a weak base. After giving Ostwald's theory of indicators, the author says, p. 138, that "the other theory of indicators is a chemical one." It is not another theory. It is a modification necessary in certain cases but not in all.

According to Hewitt "fluorescence is conditioned by a process of oscillatory tautomerism, or rapid vibration between tautomeric forms, of a peculiar kind, found among a certain class of substances capable of exhibiting what has been termed *double symmetrical tautomerism*. The two modifications absorb and emit alternately light rays of a different period," p. 148.

The reviewer is sceptical as to Plotnikow's second law, p. 152. "The second law states that photochemical action is proportional to the amount of light absorbed and is independent of the wave-length."

"The amount of light energy utilised by the leaf has been measured by Pfeffer by estimating the amount of starch produced in 1 sq. cm. of leaf surface per second of exposure and comparing the heat of combustion of the starch with the calorific effect of radiation on the same surface. According to his results only 0.6 per cent. of the total energy was absorbed, but, as the method is affected by certain serious errors, no great reliance can be placed upon the result. A very different result was obtained by H. T. Brown, who, in place of measuring the total solar energy falling on the leaf, estimated only that which was absorbed by the chlorophyll and was consequently photochemically and otherwise active. The amount of solar radiation taken up by the leaf was determined by means of a Callendar

radiometer before and after transmission through the leaf. The energy thus absorbed was found to vary in different leaves between 64 and 77 per cent.," p. 168.

"Racemisation is usually effected by rise of temperature. It was first observed by Pasteur, who obtained both racemic and mesotartaric acid by heating cinchonine *d*-tartrate to 170°. Jungfleisch modified and improved the method, heating tartaric acid with 10 to 15 per cent. of water in sealed tubes to 175° for several hours, and obtained considerable quantities of racemic and mesotartaric acid. The same process has been found to bring about the racemisation of aspartic, mandelic, isopropylphenylglycolic, and camphoric acid. Active pinene, limonene and phellandrene, active amyl alcohol, and many of its derivatives are rendered inactive by heating. Active lactic acid is converted at 150° into inactive lactide, and active quinic acid into inactive quinide," p. 200.

"When studying the action of reagents on the active chlorosuccinic acids, Walden found that by replacing chlorine by hydroxyl in the laevo compound using a strong base (potassium hydroxide or ammonia), *d*-malic acid is formed, but if silver oxide or water is employed the *l*-acid is obtained. The same thing occurs if the dextro-chlorosuccinic acid is used, that is to say, potassium gives a malic acid of opposite sign and silver oxide one of the same sign. Walden has studied the action of a variety of metallic oxides in the same way, and has shown that they form a series, the end members of which produce diametrically opposite effects in the character and amount of rotation, whilst the intermediate members form products which in sign and value lie between the two extremes. The hydroxides of the strong bases, rubidium, potassium, ammonium, copper, cadmium, barium, lead, and sodium, cause inversion of sign in different degrees, whereas those of silver, thallium, and mercury produce a malic acid having the same sign as the original malic acid," p. 206.

"Another chemical method, devised by K. H. Meyer, depends upon the rapid union of the enolic, but not of the ketonic, form with bromine. The former is unstable, and is at once decomposed with the separation of hydrogen bromide and the formation of the bromo-ketone. On adding potassium iodide the bromo-ketone is reduced, and the iodine set free is estimated by titration in the usual way. The amount of the free iodine gives that of the enol form present. A standard solution of bromine in alcohol is introduced in excess and β -naphthol immediately added in order to remove the uncombined halogen. On the addition of potassium iodide, iodine is liberated and estimated as described above," p. 373.

"Laar's tautomerism or oscillating structures, and Baeyer's pseudomerism or single, stable structures, are limiting cases of allelotropism or equilibrium mixtures of isomers. The theory which has been recently developed by T. M. Lowry has been moulded on a still broader basis. In place of the word tautomerism and the various other names applied by different observers to indicate different views of the same phenomenon, he has introduced the single expression *dynamic isomerism*, which he defines as *reversible isomeric change*," p. 388.

"At an early period in the history of the benzene formula, Kekulé put forward a dynamic hypothesis to explain the equivalence of the two ortho positions. This was followed by Knorr's oscillation formula, in which only the hydrogen atom was assumed to oscillate between each pair of carbon atoms. Knorr's view, which bears a close resemblance to Laar's theory of tautomerism, was the direct consequence of the observation establishing the identity of methyl pyrazole obtained from two different phenylmethyl pyrazoles, and has already been discussed. In 1897 a new dynamic formula was proposed by Collie, in which the carbon groups as a whole are supposed to rotate as well as change their relative positions. Without a model it is impossible to describe the evolutions of this mobile system; but it is claimed that it represents in turn the Kekulé and centric arrangement as phases of the one formula. Latterly, the study of the absorption bands in the ultra-violet region of the spectrum has led to views on the dynamical condition of benzene, which promise a very interesting development. According to Hartley, six, or according to Baly and Collie, seven, distinct absorption bands are produced by benzene. These bands are accounted for by synchronous oscillations of the molecule, in much the same way as a tuning-fork vibrates

in response to a note of definite pitch. The nature of these molecular vibrations are, however, differently interpreted by the two observers. Hartley supposes the carbons to be rotating and alternately passing through a double and single (or centric) link phase. If the passage from single to double linking produces a band, the first phase which involves the making of three double links will produce three bands and the second phase another three bands, making six altogether, though it is not obvious why the same recurrent process should produce six sets of oscillation frequencies. Baly and Collie take a different view. The oscillations are connected with dynamic change involved in the making and breaking of the links between one or more pairs of carbon atoms," p. 465.

The third volume is devoted to synthesis, the special chapters being headed: the carbohydrates; fermentation and enzyme action; the purine group; the proteins; the terpenes and camphors; the alkaloids.

"The abnormal behavior of fructose in reducing alkaline metallic salts, which is usually regarded as characteristic of aldehydes, is ascribed to the ready oxidisability of hydroxy-ketones. The case is similar to that of the hydroxy-acids, which like tartaric acid are easily oxidised and separate silver from ammonia-silver nitrate, whilst simple dibasic acids like succinic acid have no such action," p. 4.

"The conversion of one monosaccharide into another has been effected in the following way. Fischer found that on heating the monobasic acids (derived from the sugars by oxidation) in aqueous solution with pyridine to a temperature of 130°-150° a molecular change occurs. The hydrogen atom and hydroxyl group attached to the carbon atom next to the carboxyl group are interchanged and a new stereoisomeric modification is produced. It occasionally happens that the conversion is complete; but, as the process is reversible, the original and the newly formed product are as a rule present as an equilibrium mixture," p. 9.

"Lobry de Bruyn and van Ekenstein found that under the influence of alkalis, alkaline earths, sodium acetate, lead oxide, guanidine, etc., the hexoses are transformed slowly into mixtures of their isomers. Each of the hexoses, glucose, fructose, and mannose, forms under these conditions a certain proportion of the other two, together with certain other sugars, e.g. glucose, a γ -ketose, which is also found in molasses," p. 13.

"If it were possible to prepare glycollic aldehyde in quantity and build up the sugars in successive stages from it, by means of the cyanhydrin reaction, all of the stereoisomers would probably be obtained and their configuration could be determined without difficulty," p. 24.

"The discovery of the ferments concerned in gastric digestion must really be ascribed to Réaumur (1752) and the Abbé Spallanzani (1785). The latter caused birds of prey to swallow small sponges attached to a string. After withdrawal, the sponges yielded a small quantity of gastric juice which was able to dissolve and change fragments of meat. These results were, however, not accepted as correct until many years later," p. 89.

The X-ray examination of cellulose indicates unit cells containing four $C_6H_{10}O_5$ groups, p. 77. The author thinks that it is probable that haemoglobin, unlike most other proteins, forms a true solution in water, p. 155. Sodium removes an atom of hydrogen from pyridine, and dipyrindyl is formed by the linking of two molecules, p. 308.

"How is the term alkaloid to be defined? Koenigs suggested that the name, which was originally applied to all vegetable bases, including caffeine, theobromine, betaine, choline, etc., should be restricted to those vegetable products which are derivatives of pyridine only. This would exclude caffeine and theobromine, which do not differ very widely from the alkaloidal bases. In the present state of the subject an exact definition is not easy to frame, and possibly, as our knowledge grows, the line of demarcation between the alkaloids at present known and other vegetable products may become gradually obliterated. For the present, however, an alkaloid may be defined as a vegetable base which contains a cyclic nitrogenous nucleus," p. 306.

This is a remarkably interesting book. The reviewer has enjoyed immensely the reading of it. He recommends it most highly to all chemists and with especial emphasis to physical chemists. This is the kind of book they have been looking for.

Wilder D. Bancroft

The Romance of the Atom. By Benjamin Harrow. 20 × 13 cm; pp. 162. New York: Boni and Liveright, 1927. Price: \$1.50. The introductory chapters are entitled: alchemy and the dawn of chemistry; Priestley and the dawn of modern chemistry. Then follow nine chapters on the atom entitled: the atom; Mendeléeff; Crookes; Madame Curie; the energy of the future; the structure of the atom; the work of Rayleigh and Ramsay; the work of Langmuir. After this come three chapters on science and life, with the sub-heads: the origin of life; the application of science; the scientist as citizen.

In the preface the author says that "an attempt is here made to describe in non-technical language, but with strict regard for accuracy, the glorious achievements of chemists and physicists in unravelling some of the profound mysteries hidden within the atom. . . . If the magnificent work of Bohr receives but scant mention, it is because, in the first place, my primary object in writing the book was to explain, in a simple way, just what chemical action is; and this Langmuir's theory does admirably; further, to comprehend Bohr's theory requires a knowledge of physics and mathematics much beyond the grasp of the average reader. To 'popularize' Bohr's theory is not unlike the attempt to 'popularize' Einstein's theory: it cannot be done."

Wilder D. Bancroft

Lehrbuch der Thermochemie und Thermodynamik. By O. Sackur. Second edition by Cl. v. Simson. 25 × 20 cm; pp. xvi + 347. Berlin: Julius Springer, 1928. Price: 19.40 marks. The first edition of Sackur's *Thermodynamics* has been well known in its English translation for some years, and there is no doubt that it was one of the most clearly written works on the subject available. Since its appearance there have been many advances both in the theory and in the experimental results. These have to some extent been incorporated in the new edition.

It may be remarked that the useful abbreviations *cal.* and *k.cal.* for gram calorie and kilogram calorie have been adopted. The section on calorimetry is too brief to be really useful: Joly's method is mentioned without criticism and nothing is said of the new methods developed by T. W. Richards and his school. In the consideration of the experimental determination of the specific heats of gases practically all recent work, except a little carried out in Germany, is omitted, and this section is quite out of date. "Bringworth" on p. 74 should be Brinkworth. The treatment of van der Waals' equation is purely algebraical and the really difficult question of units is ignored, as it too frequently is in textbooks.

The introduction of the kinetic theory of gases in the section on the thermo-dynamics of gases is perhaps likely to be confusing and Joule's equation $(\partial u/\partial v)_T = 0$, however "strange" it may seem to the beginner, is a safer basis than the kinetic formulae, which are quite foreign to the spirit of thermodynamics. The quantum theory is introduced early but no deductions of the formulae are given. The deviations from the Debye T^3 -law observed by Onnes and his school should have been mentioned here, and not deferred to p. 321. The section on the energy of solids is otherwise excellent, although the scanty reference to lattice energy on p. 93 could have been extended with advantage, since this part of the subject is now rather prominent and is certainly interesting and capable of frequent application.

The quality of any book on thermodynamics may be estimated by its treatment of reversibility, and here the present volume is entirely satisfactory, the treatment being based on that of Planck. The inequalities for irreversible processes, however, are introduced in the usual way, yet it is questionable whether they really follow from the two laws of thermodynamics. They do, however, emerge almost automatically from the treatment of irreversibility adopted.

The applications of the two laws follow in a satisfactory way and only a few points call for comment. The rather detailed account of the applications of the Phase Rule is rather tedious and out of place, but the careful treatment of Le Chatelier's theorem is

unusual and commendable. The interpretation of the differential coefficient in the maximum work equation (4) on p. 147 is not compatible with the suffix v in the equation itself. "Activity" appears very briefly on p. 246 but no use is made of the conception. The list of values of the normal electrode potential on p. 272 is out of date and Kruger and Krummreich's very important work on absolute potentials should have been mentioned. The treatment of chemical constants and their relation to statistical mechanics is good but rather brief, and no statistical equations are actually deduced, although the relation between probability and entropy is explained in some detail. As an indication of the unusually careful treatment of the whole subject, two examples may be mentioned. The discussion of solution pressure on p. 271 makes it clear that it is not the concentration of ions *in the metal* which is concerned—a statement which almost uniformly appears or is implied in the usual textbooks when any explanation is attempted; and in the deduction of the maximum work of a gas reaction on p. 324 the external work term, $\sum n_i RT$, duly appears, as it should but rarely does.

No doubt this new edition of Sackur will be translated and so made more easily available to English and American students. If this is done some of the omissions mentioned might usefully be made good, the International Critical Tables turned to account and the literature references extended so as to cover more of the recent English and American work than seems to have been available to Dr. Simson, who has otherwise done her work extremely well. The book is one which can be read with profit by all students of chemistry.

J. R. Partington.

Laboratory Glass Blowing. By *F. C. Frary, C. S. Taylor, and J. D. Edwards.* 21 × 15 cm; pp. viii + 116. New York: McGraw-Hill Book Co., 1928. Price: \$1.50. This book was first published in 1914 as "Laboratory Manual of Glass Blowing" and has now been altered and supplemented particularly in reference to Pyrex glass which has come into such wide use since that time.

The purpose of the book is stated, "to provide a clear and detailed discussion of the elements of glass working." These elements are wisely held to include those operations which the scientific worker may be called on to perform in the manufacture and repair of simple glass apparatus.

The chapters are entitled: glass and its working characteristics; general operations; elementary exercises; advanced exercises; modified methods and special operations; glass-to-metal seals and joints. Under these headings are discussed such subjects as: devitrification; annealing; types of glass and their properties; the arrangement of equipment; cleaning and cutting glass; operations on tubes; capillary tubing; joints and repairs on apparatus; ground joints; vacuum tubes; sealing glass to Pyrex, porcelain, platinum, and base metals. The appendix gives formulas and directions for use of; platinizing solutions, stop-cock lubricants, vacuum wax, deKhotinsky cement, cement.

The book is well written and succeeds in imparting a great deal of information. The operations are arranged in just about the same order as that followed by expert glass workers in their instruction to apprentices and the descriptions of these operations are detailed enough for ease in carrying them out. In addition, many of the procedures are well illustrated by drawings showing each step. It is anticipated that this little book will be welcomed as a valuable aid by that army of laboratory workers who have some skill and much ambition to do things with glass.

Herbert L. Davis.

CALCITE AND ARAGONITE

BY CHARLES HAMILTON SAYLOR

Introduction

Although aragonite is metastable under all geologic conditions,¹ it is a mineral of common occurrence. Many sea-shells are composed entirely or in part of aragonite, the pearly layer of most mollusk shells being aragonite. The oyster can, with certainty, produce a uniform layer of this metastable modification of calcium carbonate at temperatures where no man has produced it in any purity. But despite the tons of aragonite present in many mineral deposits, there has been no satisfactory explanation of its formation. An effort has been made to use Ostwald's law of successive states, but it can be seen how inadequate this is if we merely reword the law to read: "If a metastable phase appears in any transformation, it precedes the stable phase, since no subsequent transformation can be from the stable to the metastable form." It is perfectly clear that no metastable form can succeed a stable modification, but why it should ever precede it has been left unanswered. In order to treat this general problem of the formation of metastable, indeed in many cases monotropic, modifications, and the particular problem of aragonite and calcite, it was deemed wise to learn more about a number of simpler crystallization phenomena.

When calcium carbonate appears as aragonite instead of as calcite, there is more than a mere change of external form. The entire structure of the crystal is altered; there is a change of crystal system and an entire rearrangement of atoms within the crystal. By learning all we can about changes of crystal form when there is no internal rearrangement we shall place ourselves in a better position to understand the more complex problems of calcite and aragonite.

Sodium chloride crystallizes from pure aqueous solution only in cubes, but the mineral halite occurs occasionally in small octahedra as well as in cubes. Hatty² observed that when the solution from which salt crystallized contained urea, he could duplicate the naturally occurring octahedra. Many other foreign substances have similar effects. In all such cases, however, the crystals are still practically pure sodium chloride and the formation of complex compounds in solution cannot directly explain the anomaly.

The most obvious assumption is that urea is adsorbed preferentially on certain crystal faces, thereby changing their rate of growth, but a direct proof of the particular faces upon which urea is adsorbed presents enormous analytical difficulties. The problem can, however, be solved by an indirect method. If we have any substance which can crystallize from aqueous solution in two forms, and we let it crystallize once in the presence of a

¹ Bäckström: *J. Am. Chem. Soc.*, 47, 2432 (1925).

² "Traité de mineralogie," 2, 356 (1801).

presumably strongly adsorbed cation and the second time in the presence of a presumably strongly adsorbed anion, one or the other of the two solutions will show an increased tendency to give the less stable crystal habit. As starting solutions we would naturally choose acids and bases, or acid and basic dyes. If the less stable form appear, let us say, in alkaline solutions, we can predict that all strongly adsorbed anions will tend to produce the same effect, and that all strongly adsorbed cations will tend to counteract that effect.

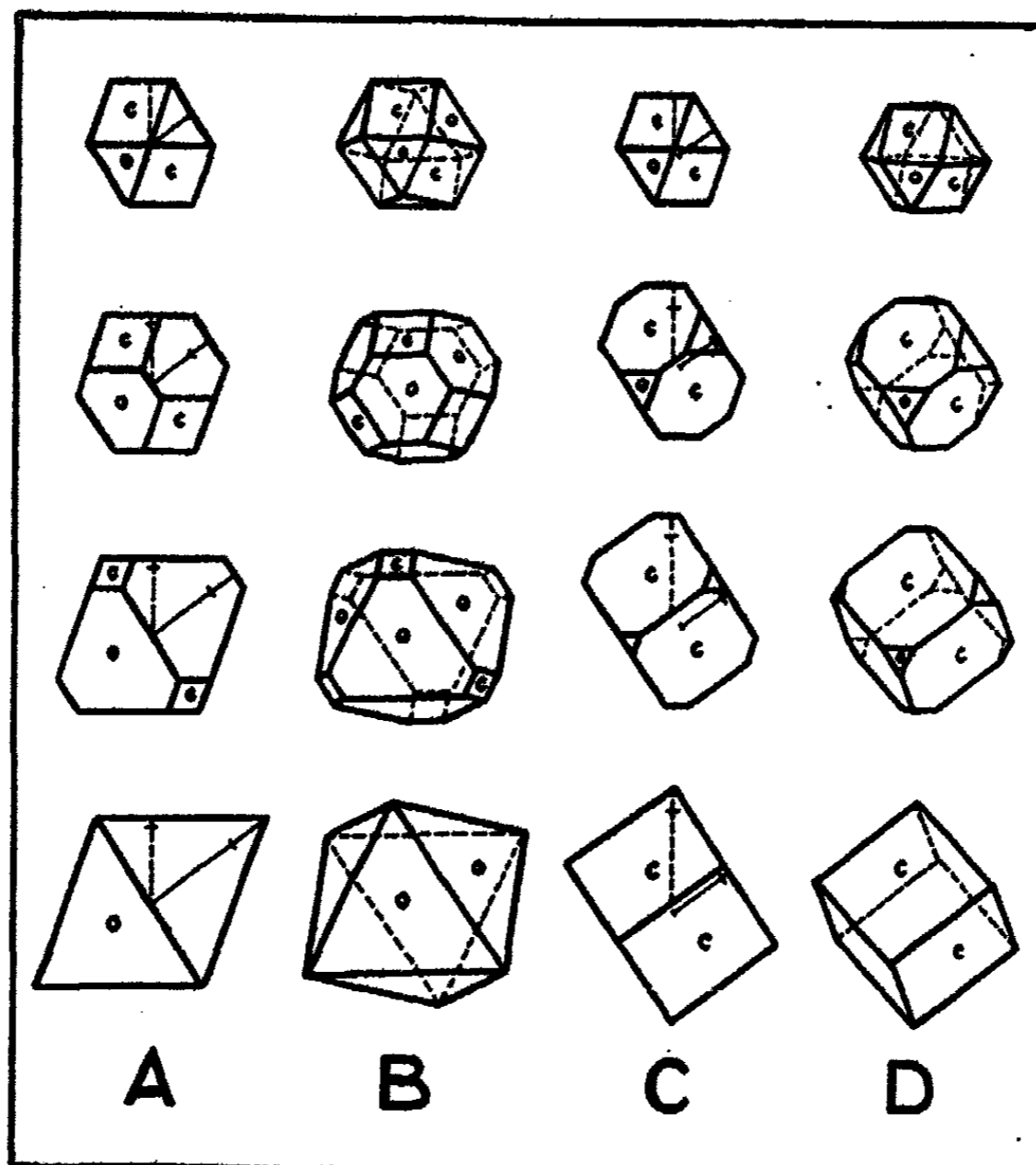


FIG. 1

Starting in A and B with crystals where cube and octahedron faces are equally developed, growth perpendicular to the octahedron face is represented four times as fast as growth perpendicular to the cube face. The octahedron gets smaller in extent and ultimately disappears. In C and D, growth perpendicular to the cube face is three times as fast as growth perpendicular to the octahedron face. The cube gets smaller and ultimately disappears. Series A and C have been chosen so that the perpendicular distance to each crystal face lies in the plane of the paper. The distance to a cube face is drawn as a full light line; to an octahedron face as a light dotted line. The previous extent of the crystal is marked by a small cross on these lines. Series B and D make clearer the shapes of the crystals represented in Series A and C.

It is known experimentally that sodium chloride crystallizes from hydrochloric acid solutions in cubes, just as it does from pure water, while the presence of alkali favors production of octahedron faces. We therefore

deduce that the adsorption of anions favors the development of octahedron faces on sodium chloride, and that urea is adsorbed on the same faces that anions are. It will be shown that this assumption enables us to predict the effect of many other additions to sodium chloride solutions and that this new technique is absolutely general, applying to all substances crystallized from solution or melt and leads ultimately to a full explanation of the calcite and aragonite difficulty.

To favor a crystal face, adsorption must occur on that face. The flat side of a pea is the side where it has been prevented from growing by nearness to its neighbor. An octahedron, a cube, or any other crystal face is a flat side on the crystal. When adsorption occurs on the eight corners of the cube, the ions of the crystalline substance must first displace the adsorbed material before they can become part of the crystal structure. The filling out of the eight corners is retarded, and eight flat places, the eight faces of the octahedron, develop. Similarly a substance adsorbed along the twelve edges of the cube would cause flat places to develop there. They are the twelve faces of the dodecahedron. In the same way, from the six corners of the octahedron we get the six cube faces, and from the twelve edges, the twelve dodecahedron faces.

The structure of the sodium chloride crystals is face-centered cubic,¹ oppositely charged ions being displaced half a unit parallel to the sides of the unit cell. This is the structure most commonly named merely the "sodium chloride structure." An important characteristic is that crystal planes parallel to any cube face have a checkerboard arrangement of alternating sodium and chlorine ions, that planes parallel to an octahedron face are composed of only one kind of atom, sodium and chlorine existing in alternate planes, that planes parallel to a rhombic dodecahedron face are composed of alternating rows of sodium and chlorine. Niggli² employing this structure and the probable forces of attraction between a growing crystal and its mother liquor, formulates the mechanics of crystal growth. From his argument there follows naturally the answer to the question, "Why does a crystal have faces anyway?" The surface of the crystal fragment that is slightly oblique to an atomic plane will be a series of atomic steps. A sloping irregular surface will grow perpendicular to itself more rapidly than adjacent atomic planes, until it fills out to their position. After that the crystal will be bounded by crystal faces. Further, in a crystal of the type of sodium chloride, perpendicular to a cube face with its equal number of positive and negative particles, the electrostatic field attracting new ions will presumably be slight and a comparatively low rate of perpendicular growth will follow. Perpendicular to an octahedron face on the other hand the residual electric field will be enormous and crystal growth will tend to be extremely rapid. A compensating influence, that Niggli neglected, occurs in that only one kind of atom at a time can add itself to the octahedron face. The perpendicular growth of

¹ Wyckoff: "The Structure of Crystals," 304 (1924).

² Z. anorg. allgem. Chem., 110, 55 (1920).

the octahedron face is retarded by alternate impoverishment of the region first of sodium and then of chlorine ions. Therefore, although the octahedron face has the strongest electric field, its rate of growth is intermediate between the cube and other forms.

Spangenberg,¹ Valetton,² Miss Bentivoglio³ and others have measured rate of growth of crystals from the pure mother liquor. Employing a sphere of potassium alum, Spangenberg witnessed the appearance of many faces not ordinarily observed with alum. Perpendicular to each crystallographic plane, under standard conditions there is a characteristic growth velocity. The velocity of growth is unusually high in directions perpendicular to planes of incommensurable indices. Such surfaces disappear quickly. The alum crystal is then bounded by a large number of slower growing crystal planes, which in turn tend to disappear in the approximate order of growth perpendicular to their surface. This does not, however, hold exactly. If the perpendicular distance from the center of an octahedron to a face is unity, the distance to a corner (where the cube appears) is 1.7321 and to an edge (where the dodecahedron appears) is 1.2247. Clearly, the dodecahedron will disappear before the cube if both have the same rate of growth. The dodecahedron can even have a slower growth until the ratio 1.2247 to 1.7321 is reached and yet disappear first. To borrow a biological term, the cube is more distal on the octahedron than the dodecahedron. Conditions will be exactly similar when any two forms compete against a still slower form. The discrepancies between the rates of growth of different forms are usually great enough, however, that faces disappear in the order of their growth velocity.

Employing the isomorphous salts, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, Miss Bentivoglio found that the ratio of growth velocity for different forms varied widely in different members of the series. The rate of growth, therefore, is not related in a simple way to reticular density nor is the residual electric field the sole factor governing crystal growth even from pure solutions. Even when a substance crystallizes from its pure solution it is probable that adsorption upon the crystal of solvent and solute alters and serves to modify its external form.

Marc⁴ in a classical series of researches, studied the influence of foreign substances upon crystal growth, and reached the conclusion that foreign materials alter the external form of a crystal only when selectively adsorbed and that adsorption upon a crystal always retards its growth. Marc's most conclusive results came from the adsorption of dyes upon crystals. Gaubert⁵ dyed crystals and considered the formation of dye and crystal laminae as the essential factor modifying crystal form. Reinders⁶ studied the relation between the adsorption of dyes upon silver chloride and the formation of

¹ Z. Krist., 61, 189 (1925).

² Z. Krist., 59, 335 (1924).

³ Proc. Roy. Soc., 115A, 59 (1927).

⁴ Z. physik. Chem., 61, 385 (1908); 67, 470 (1909); 68, 104 (1909); 73, 685 (1910); 75, 710 (1911).

⁵ "Le faciès des cristaux," (1911) pamphlet; and Compt. rend., 157, 1531 (1913).

⁶ Z. physik. Chem., 77, 677 (1911).

dendritic crystals. Walcott¹ grew crystals of lead, strontium and barium nitrates in the presence of a large number of inorganic salts, and concluded, without reason I think, that adsorption was not the principal factor modifying crystal form. Since salts of relatively low solubility seemed to have the greatest effect, Walcott decided that the solubility of the added substance was the governing property. If he had observed the profound influence of nitric acid, his conclusions might have been different. Keenan and France² measured the relative rates of growth of the two principal faces upon potassium alum crystals, both when crystallized from pure solutions and from solutions containing as high as .05% of various dyestuffs.

Keenan and France hold the opinion that adsorption is the governing influence when foreign substances alter crystal form, but decide that adsorption is altogether specific and that nothing can be predicted about it. Indeed their experiments would at first seem to justify this conclusion. One basic dye and one substantive dye decreased the growth of the cube relative to the octahedron. All other dyes tried were without effect. They conclude therefore that the adsorption of dyes upon the cube face is the result of a specific interaction between the crystal and the dye, that it is a property of the chemical nature of each and of nothing else.

Clearly the influence of foreign substances upon crystal form is pretty much up in the air. Walcott considers it a matter of the slight solubility of the foreign substance; Spangenberg³ postulates a complex, hydrated, sodium-urea cation as the cause of formation of octahedra upon sodium chloride; Reinders presents data which are useless as touching upon the general theory; Keenan and France study the effect of dyes upon potassium alum and decide that adsorption is the governing factor, but that nothing is known about the adsorption. In this paper the problem has been made general, and by the employment of simple and usually qualitative experiments, its inconsistencies reconciled.

It will be shown in the following pages that foreign substances are adsorbed preferentially upon certain crystal faces. The growth of faces perpendicular to themselves is retarded when adsorption occurs. New material to build the growing crystal must diffuse through and displace the adsorbed substance. It can usually do this, but rapid addition of ions or molecules to the growing crystal face will be prevented. Sometimes the adsorption is so great as virtually to stop all growth. In these cases the adsorbed substance is held permanently on the crystal and often found as inclusions within the crystal. At other times adsorption is less marked and there can be no direct proof of the adsorption. The adsorbed substance is displaced without great difficulty by the crystal material and the growth of the face perpendicular to itself is but slightly retarded. Always, by slowing the perpendicular growth of a face, adsorption tends to make that face become larger. It becomes a

¹ Am. Mineral., 11, 221, 259 (1926).

² J. Am. Ceram. Soc., 10, 821 (1927).

³ Z. Krist., 59, 375 (1924).

larger flat place upon the crystal. I shall further show that the same generalization can be made about adsorption upon a crystal face as can be made about adsorption upon anything else, that this adsorption follows the same rules that are followed in all adsorptions. Frequently a non-ionized substance—as urea—is adsorbed, but it is adsorbed in the same way as if it were an ion. It is a necessary conclusion that molecules of the solvent may also be adsorbed. This often causes isomorphous substances to have entirely different external forms. Similarly, the shape of a substance is not necessarily the same when crystallized from different solvents, or when sublimed. Hydrogen and hydroxyl ions are usually more strongly adsorbed than other ions. Using acid and alkaline solutions, their influence upon external crystal form has served as a key to the entire field of adsorption and has tied in with those examples where adsorption can actually be demonstrated. This new technique is absolutely general; it applies to all crystal systems; it applies to crystals growing from solvents other than water; and it can be applied to crystals growing from a melt if the chemistry of the melt is understood sufficiently.

Experimental Part

Saturated salt solutions were prepared by shaking salt with water at a temperature a little above that of the room. These solutions were cooled and allowed to stand at room temperature, no particular effort being made, however, to ensure exact equilibrium. Usually foreign substances were added to the solvent before saturating with the salt. This was the most profitable time, since many of them greatly influence the solubility of the salts in water. A drop of solution was then placed upon a microscope half-slide and crystals grown by allowing the solution to evaporate at room temperature. Meanwhile the growing crystals were observed with the microscope. Frequently it was advisable to grow larger crystals. The solution, made unsaturated by the addition of a few drops of water, was placed in a clean crystallizing dish, covered with a piece of smooth paper, and put in a quiet place for isothermal evaporation. Usually, however, crystals were grown upon a slide and observed with a microscope. Most crystals prepared in this way reached a diameter of about fifty microns.

It has often been reported that occasional crystals of sodium chloride grown from pure water have octahedron faces, truncating the corners of the cube. There is no apparent reason why, if this is ever true, it should be so rare. A drop of saturated sodium chloride solution was placed upon the slide and allowed to evaporate. No crystals with any octahedron faces were observed, although the procedure was repeated many times. When, however, a crystal has been tilted so that a corner of the cube is nearest the slide, an irregular triangular surface develops there. Such a crystal might easily be mistaken by a careless observer for an octahedron, as will be apparent from Fig. 2. A drop of solution upon a slide is boiled to dryness over a micro flame. More water is added and the boiling repeated. After several such evaporations crystals grown from the same preparation will have octahedron faces

truncating the corners of the cube. Obviously a small amount of alkali has dissolved from the glass slide. Two suggestions, therefore, are offered as possible explanations of sodium chloride octahedra that have been described as crystallizing from pure water¹ or from solutions containing nickel chloride, ferric chloride, or hydrochloric acid. The present writer has been unable to obtain any true octahedron faces upon salt crystals grown in such media.

Sodium chloride crystals were grown from solutions containing 10% and 20% sodium hydroxide. From the 10% solution the crystals were cubes,

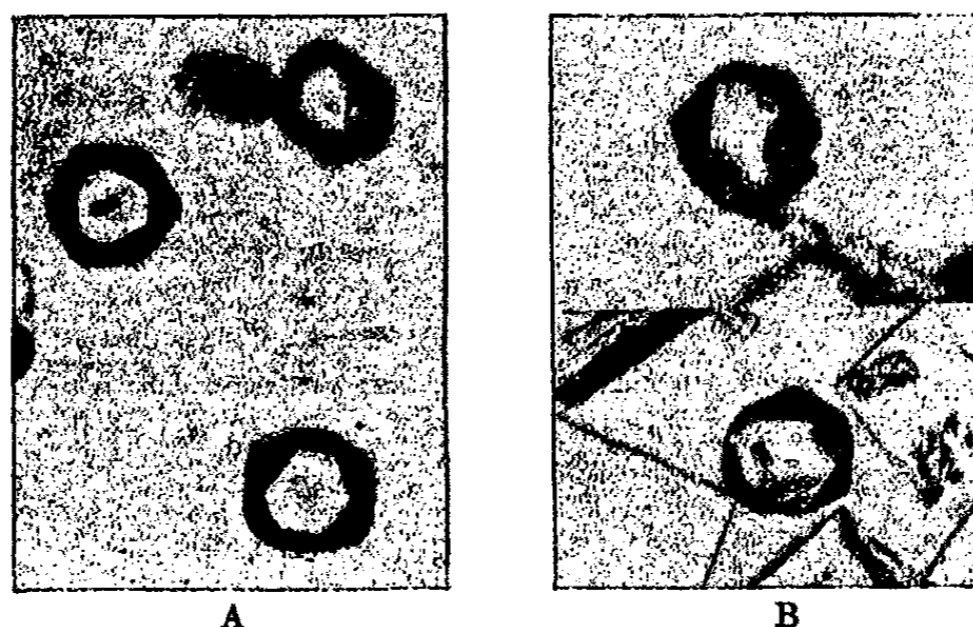


FIG. 2

- A. True octahedra of sodium chloride grown in the presence of urea.
 B. False octahedron. A triangular corner of the cube, floating in the surface of the liquid, is prevented from growing. The outlines of the under side can be seen through the crystal.

the corners being truncated by tiny octahedron faces. From the 20% solution the truncations are much larger, but the octahedron is in no case the dominant form. Other alkalis were used in similar concentrations. Potassium hydroxide yielded results identical with sodium hydroxide. Ammonium hydroxide introduced difficulties since it was hard to know its concentration at the time of crystal formation, but by starting with a strongly ammoniacal solution the corners of the salt crystal were cut by octahedron faces. A solution to which had been added sodium carbonate almost to saturation grew crystals of sodium chloride, cubes with small octahedron faces at the corners.

Solutions were prepared containing several concentrations of hydrochloric acid, sulphuric acid, phosphoric acid, nickel chloride, and ferric chloride. All crystals grown from these solutions were cubes. The octahedron face never appears.

Antimony trichloride, in solutions containing hydrochloric acid, gives to a certain extent ions of the acid² H_3SbCl_6 . This anion is strongly adsorbed on the octahedron face when sodium chloride is crystallized in its presence, and so it favors formation of octahedra. Microscopic crystals exhibit incurved

¹ Orloff: *J. Russ. Phys. Chem. Soc.*, 28, 715 (1896); abstracted in *Z. Krist.*, 31, 516 (1899).
² Abegg: "*Handbuch der anorganischen Chemie*," 3 (III), 589 (1907).

octahedron faces and no cube faces. Strong adsorption is probably favored by the simultaneous adsorption of hydroxyl ions from water on the same crystal faces. The antimony then precipitates as a basic salt and the combined adsorption results in plating an insoluble layer upon the octahedron face. This effect is so marked that, when crystals are grown rapidly to relatively large size, the antimony is present as inclusions within the crystal. The inclusions take the form of a milky pyramid, opening out fan-wise to the octahedron face. This milky pyramid is conclusive experimental evidence that adsorption occurred on the octahedron face during its formation.

Urea is not the only non-electrolyte which is preferentially adsorbed like an anion upon the octahedron face of sodium chloride. When sodium chloride is crystallized from a solution containing 5% mercuric chloride, crystals are octahedra with cube faces at the corners. From a solution containing 15% of glycocoll the crystals are mixed octahedra and cubes, the octahedra predominating slightly. We see, then, that the development of octahedron faces on sodium chloride is favored in solutions containing readily adsorbed anions, of which hydroxyl ion is the most easily controlled, and in solutions containing a certain group of non-electrolytes. A similar group of cations must be adsorbed upon the cube face and tend to stabilize it. Since the cube is stable anyhow this tendency has no visible result.

Alcohol decreases Adsorption of Anions

It is well established that alcohol tends to decrease the adsorption of anions. Bancroft¹ writes that "colloidal platinum is charged positively in aqueous alcohol though negatively in pure water. There seems to be no special reason why the effect of alcohol on platinum should be specific and it seems to be true experimentally that alcohol tends to precipitate negatively charged sols, being more effective if the sol has been made relatively instable by the addition of electrolytes. The negatively charged globules in rubber latex can be precipitated by alcohol in the presence of salts." Gurchot² coagulated negative sols of copper ferrocyanide, arsenious sulphide, and sulphur with ethyl alcohol, the coagulation being more marked when a coagulating salt was also present though in insufficient amounts to cause precipitation itself. Klein³ observed no agglomeration of positively charged ferric oxide by alcohol.

Since alcohol decreases the adsorption of anions, we can predict that it will tend to counteract the effect of anions, urea, and other non-electrolytes which favor the formation of octahedron faces on sodium chloride. To test this prediction ten percent of alcohol was added to each solution, and the experiments with sodium chloride repeated. The results listed in Table I show that alcohol does counteract the tendency to form octahedra. They furnish a striking confirmation of our primary postulate that anions are adsorbed on the octahedron faces and that non-ionized substances which favor octahedra do so because they are adsorbed as if they were anions.

¹ "Applied Colloid Chemistry," 263 (1926).

² J. Phys. Chem., 30, 83 (1926).

³ Kolloid-Z., 29, 247 (1921).

TABLE I

| Foreign Substance | Crystallization of Sodium Chloride | |
|----------------------------------|------------------------------------|----------------------------------------|
| | Without alcohol | With 10% ethyl alcohol |
| 10% NaOH | Cubes, small octahedron faces | Cubes |
| 20% NaOH | Cubes, large octahedron faces | Cubes, octahedron rare |
| 20% HCl | Cubes | Cubes |
| 5% Urea | Cubes, large octahedron faces | Cubes |
| 15% Urea | Octahedra | Cube-octahedron |
| 10% Glycocoll | Cubes, large octahedron faces | Tendency to octahedron greatly reduced |
| 5% HgCl ₂ | Cube-octahedron | Cubes, small octahedron faces |
| H ₃ SbCl ₆ | Octahedron | Cube-octahedron |
| FeCl ₃ | Cubes | Cubes |

No additional experiments were performed with potassium hydroxide, ammonium hydroxide, or sodium carbonate or nickel chloride. An attempt was made to observe the influence of acid and basic dyes, but a saturated solution of sodium chloride precipitates dyes completely. Methyl violet, a basic dye, Soluble Blue 3 M, Nap Black 12 B, Coomassie Fast Black B, Alkali Blue and Disulphine Blue A, acid dyes (British Dyestuffs Corporation), were tried, but in all cases the dye is insoluble in the strong salt solutions.

Application of the Method to other Substances

Since our technique is general, it was next applied to a number of other substances. Take, for example, the case of potassium alum. It crystallizes ordinarily in octahedra, but it can be crystallized as cubes from weakly alkaline solutions—from solutions containing potassium carbonate or borax.¹ Hydroxyl is adsorbed not on the octahedron faces of alum, but on the cube faces. We can predict that other anions, urea, and glycocoll will also be adsorbed on the cube faces, and produce cubes. Acid solutions and all cations, in the degree that they are adsorbed, will stabilize the octahedron. Alcohol will decrease the adsorption of anions and tend to neutralize the effect of alkali. Experiments in this line are summarized in Table II.

TABLE II

| Added | Potassium Alum Crystallization | |
|----------------------------------|--------------------------------|-----------------------------------|
| | Without alcohol | With 10% ethyl alcohol |
| Potassium carbonate | Cube and octahedron | Disappearance of cube |
| Borax | Cube and octahedron | Disappearance of cube |
| H ₃ SbCl ₆ | Very large cube faces | Cube faces relatively smaller |
| Urea | Cube faces large | Effect of alcohol less pronounced |

¹ Rinne: "X-rays and the Fine Structure of Matter," 136 (1925); Le Blanc: "Crystallographic" (1808).

When potassium carbonate or borax was added to alum solutions there was a light flocculent precipitation of hydrated aluminum oxide, but this only interferes with the experiment by limiting the possible alkalinity of the solution. These results indicate clearly that anions and substances that simulate anions are adsorbed, not upon the octahedron faces, as with sodium chloride, but upon the cube faces. Their adsorption is decreased by the presence of alcohol in solution. Potassium alum will be considered in another relation in the following pages.

Barium nitrate crystallizes ordinarily in octahedra,¹ but Gaubert² and Walcott³ have observed that when it is crystallized from solutions containing methylene blue, cube faces develop, and that they are often colored by the dyestuff. Methylene blue is a true basic dye and has therefore a strongly adsorbed cation, the color base which by adsorption on the cube face favors that habit. The concentrated barium nitrate solution has less tendency to precipitate the basic dye than sodium chloride had to precipitate dyes because of the leaching action of barium ion. Briggs and Bull⁴ have shown that the amount of methylene blue adsorbed by wool from alkaline solutions is cut down to about one-half when the dye bath is 0.01 N with barium chloride. Barium tends therefore to keep the dye in solution. Acids would have the same effect. Methylene blue is adsorbed, therefore, strictly as a cation. It is not, as will be found later with sodium fluoride, a mordanting action of the ions of water. Since the dye cation is adsorbed on the cube face, we are enabled to predict from this single key reaction what other readily adsorbed substances will do. Barium nitrate shows even from pure water a certain tendency to form cube faces at the corners of the octahedron. We can predict that hydroxyl ion and urea will suppress that tendency, as we find they do. We can further predict that nitric acid will act like methylene blue, the hydrogen ion by adsorption on the cube favoring it. Experiment confirms our prediction. The cube is so strongly favored that crystals grown from acid solution look more like crystals of sodium chloride than of barium nitrate. They are cubes with the slightest octahedron truncation. Since in this case it is a strongly adsorbed cation which is effective, we expect alcohol to be without marked effect, as indeed, experiment shows. On the other hand urea should tend to counteract the effect of nitric acid. Parallel experiments where barium nitrate is crystallized from solutions that contain nitric acid and from solutions that contain the same amount of nitric acid and twenty percent of urea were performed. In both experiments there were eight cubic centimeters of concentrated nitric acid per hundred cubic centimeters of

¹ There is a certain doubt as to whether they are really octahedra or \pm tetrahedra equally developed, but for our purposes that is immaterial. The most modern data from crystal structure determinations indicate that opposite faces are alike. In that case it is correct to call them octahedra.

² "Le faciès des cristaux," 13 (1911).

³ Am. Mineral., 11, 272 (1926).

⁴ J. Phys. Chem., 26, 845 (1922).

solution. Solutions containing no urea give cubes as the ordinary form; but, only octahedra are developed when urea is present. Urea, therefore, opposes the influence of hydrogen ion.

Sodium nitrate crystallizes in the hexagonal system. It is rhombohedral hexagonal. Crystallized from pure water, it forms moderately long, six-sided, needles with six-sided pyramids at the ends (actually a form of rhombohedron). If we let it crystallize once in the presence presumably of a strongly adsorbed cation, and then in the presence of a presumably strongly adsorbed anion, one should be adsorbed on the pyramids and make short stubby crystals, the prism practically disappearing. The other should be adsorbed on the prism faces producing long, thin crystals. Experimentally we find that nitric acid produces this latter effect. From this we can reasonably predict that sodium hydroxide, by adsorption of hydroxyl ion on the pyramid faces will produce the short stubby crystals, which it does.

Difficulties were encountered temporarily with potassium chloride. In all cases we have employed acid and basic solutions as a key to the action of other substances, considering that urea, glycocholl, and mercuric chloride, which are not or only slightly ionized, would act like hydroxyl ion, and that hydrogen ion would have an opposite effect. The concentration of potassium hydroxide was varied from 5% until the solution was nearly saturated with both hydroxide and chloride, but the crystals were always cubes. Hydrochloric acid was varied in similar manner, but still the crystals were always cubes. Since the structure of potassium chloride is identical with sodium chloride, it is reasonable to suppose the possible existence of an analogous octahedron face. Actually some natural crystals of sylvite exhibit the form. According to our initial postulate either acid or basic solutions should favor octahedra, one or the other. The problem was temporarily complicated further when it was found that potassium chloride grown from an 18% solution of urea had octahedron faces, and crystals grown from 30% urea were octahedra. Potassium hydroxide should have this same effect, but it has not, probably because selective adsorption is not sufficiently strong.

The corner of a cube is $\sqrt{3}$ times as far from the center of the figure as the middle of the cube face. Consequently as long as the rate of growth perpendicular to the octahedron face divided by the growth perpendicular to the cube face is greater than 1.732, the octahedron will never be a form upon the crystal and the amount of the discrepancy will have no outward effect. We can, however, decrease the rate of growth of the octahedron with a substance like urea. Potassium hydroxide should tend to have the same effect, and, in a mixed solution, the effects should be more or less additive. If we start with a solution of potassium chloride that contains just enough urea to give small octahedron faces, the addition of potassium hydroxide to the solution should enhance the tendency to form octahedra. If alcohol is also included, it will decrease this tendency and give us cubes again. Table III shows how well this is borne out.

TABLE III
Crystallization of Potassium Chloride

| HCl | Glycocoll | KOH | Urea | Alcohol | Crystals are |
|-----|-----------|-----|------|---------|-------------------------------|
| 20% | — | — | — | — | cubes |
| — | 20% | — | — | — | cubes |
| — | — | 10% | — | — | cubes |
| — | — | — | 12% | — | cubes |
| — | — | — | 18% | — | cubes, small octahedron faces |
| — | — | 10% | 18% | — | octahedra, small cube faces |
| — | — | 10% | 18% | 10% | cube, octahedron |

Experiments with Acid and Basic Dyes

Dyes are insoluble in saturated solutions of sodium chloride and potassium chloride, but there are two halogen salts of an alkali metal with which better results can be expected. Sodium fluoride was chosen since its solubility is low enough so that the saturated mother liquor is not a strong solution and it is not, like lithium fluoride, so insoluble that crystal growing is difficult. One hundred cubic centimeters of water dissolve 4.22 gms of sodium fluoride at 18° C. Solutions of the salt were prepared in platinum vessels and crystals grown upon a celluloid slide, since solutions of the fluoride attack glass with fair rapidity. An orientation group of experiments is indicated in Table IV.

TABLE IV
Crystallization of Sodium Fluoride

| Solution contains | Crystals are |
|----------------------|---------------------|
| no foreign substance | cubes |
| glycocoll | octahedra |
| urea | octahedra |
| NaOH | octahedra |
| NaOH + alcohol | cube and octahedron |

Smaller amounts of alkali, urea, and glycocoll were needed to produce a pronounced change in the form of sodium fluoride than with any other substance studied. There is very strong adsorption upon the octahedron faces of sodium fluoride. Alcohol reduces this adsorption and favors the retention of cube faces. Unless very small amounts of urea, glycocoll, or sodium hydroxide are used, crystals grown in their presence are covered with a cloud of jelly-like material, but with the smaller amounts of the added substance, crystals are well defined.

The crystal form of sodium fluoride is subject to the same controlling influences as sodium chloride and potassium chloride. Anions and non-electrolytes which resemble anions in their effect are adsorbed upon the octahedron face and favor that form. If it had been possible to crystallize

the two chlorides in dye solutions we have every reason to believe that the results would have been identical with those which follow for sodium fluoride. Solutions of sodium fluoride were prepared containing the acid dyes Soluble Blue 3 M, Nap Black, Coomassie Fast Black B, Disulphine Blue A, and the basic dyes methyl violet and malachite green. The acid dye Alkali Blue is precipitated even by the sodium fluoride solution, and could not be employed. The concentration of dyestuff was sufficient in every case plainly to color the drop of solution on the celluloid microscope slide, but not to any deep shade. None of the dyes employed modified in any degree the form of the crystal, but the dyes fell sharply into two groups when it came to coloring the crystals. All the acid dyes colored the cube faces, Soluble Blue 3 M, Nap Black 12 B, and Disulphine Blue A coloring them blue and Coomassie Fast Black B coloring them violet. As the crystallization continued, all of the dye was removed from solution. Basic dyes on the other hand did not affect the crystals in any degree, and all of the color remained in solution. It is easy to arrive at the explanation of why acid dyes color the cube faces of this salt, and why basic dyes remain in solution. We have shown that alkalis favor the development of octahedra and from this deduce that hydroxyl ion is preferentially adsorbed on the octahedron face. A corollary of this is that hydrogen ion is preferentially adsorbed on the cube face where it should have a mordanting effect on the acid dye. Since there was no distinction between different acid dyes, this is probably what happened. Basic dyes, on the other hand, were not taken up by the crystals. The crystals have no octahedron faces to adsorb hydroxyl ions and mordant the basic dyes. A foreign substance which will cause the development of octahedron faces by being itself adsorbed, should permit adsorption of hydroxyl ions on the newly formed faces, and thus favor the mordanting of basic dyes. Urea cannot be used, probably because it is so strongly adsorbed that it prevents other adsorption. Four percent of sodium hydroxide causes approximately equal development of the cube and octahedron faces. The alkali precipitates the greater part of the basic dye from solution so that results are less brilliant than with acid dyes, but octahedron faces are colored a faint pink by magenta and a pale wine color by methyl violet. These basic dyes, therefore, are mordanted upon the octahedron faces by hydroxyl ions already adsorbed.

The manner in which acid and basic dyes are taken up by sodium fluoride forces one's attention to the rôle which adsorbed solvent must play in the modification of crystal form. In this example for the first time we can show the adsorption of the ions of water itself. That adsorption has been sufficient to mordant dyes. Urea a non-electrolyte is strongly adsorbed and changes the crystal habit. It seems likely that the habits of crystals grown from pure solvents are largely influenced by adsorption of the solvent upon particular crystal faces.

Apparent Inconsistencies

It has already been mentioned that Keenan and France,¹ from work upon potassium alum, had decided that the adsorption of dyes upon crystals

¹ J. Am. Ceram. Soc., 10, 821 (1927).

is altogether specific and obeys no known laws. They grew alum from solutions containing a number of acid dyes, e.g. naphthol yellow and quinoline yellow, the basic dyes methyl violet, methylene blue, and Bismarck brown, and the substantive dye Diamine Sky Blue FF. Only Diamine Sky Blue FF and Bismarck brown colored the crystals or modified to any marked extent the crystal form. There is, of course, no way of telling what action the substantive dye will have, but it is a little striking that Bismarck brown behaves so differently from the other basic dyes. Inasmuch as the writer had encountered difficulties because strong salt solutions precipitate most dyes, it appeared highly probable to him that Keenan and France had not worked with a true solution of dyes but with precipitated dyes that were nevertheless suspended in the solution. Collodion dialysis membranes were prepared in the usual manner. On the inside were placed saturated solutions of potassium alum, to each one hundred cubic centimeters of which had been added .05 gms of methyl violet, methylene blue and Bismarck brown. On the outside of the membranes were placed saturated solutions of alum. Methyl violet and methylene blue dyed the membrane so that no reliable data could be obtained. In order to determine whether the dyes are in true solution another method must be employed. Saturated alum solutions containing .05 gms of naphthol yellow, Diamine Sky Blue FF (Chlorazol Sky Blue FF), methyl violet, methylene blue, Bismarck brown, and potassium permanganate as a check were placed in different test tubes. The test tubes were fitted with rubber stoppers through which passed glass tubes three millimeters in internal diameter and two decimeters long. These tubes were sealed at the upper ends, filled with pure saturated potassium alum solution, and carefully inverted so that the open ends were just immersed in the liquids in the test tubes. After two days in a quiet dark place, the potassium permanganate had diffused to the top of the up-turned tube of colorless solution. Methyl violet, naphthol yellow, and methylene blue had also diffused to the tops of the tubes, but Diamine Sky Blue had diffused only six centimeters and Bismarck brown a mere seven millimeters. Diamine Sky Blue FF, as we know in advance since it is a substantive dye, and Bismarck brown are not in true solution in saturated alum solutions. The dyes which are in true solution do not alter the crystal form of potassium alum. This confirms the results with sodium fluoride, dyes in true solution being in some cases mordanted on the crystal, but not influencing the crystal form. The experiments by Reinders upon silver chloride crystallized from solutions containing dyes present an immense number of irregularities that make a full understanding of the adsorption mechanism in that case rather difficult. It must be remembered, however, that Reinders prepared the crystals by dissolving silver chloride in ammonium hydroxide and growing crystals from that solution. As a general thing, basic dyes colored the crystals more strongly than acid dyes, but some acid dyes caused a tinting of the crystals. We can explain Reinders' results if we assume, for want of experimental evidence, that silver chloride octahedra grown from pure water take up acid dyes. By growing crystals in alkaline solution then hydroxyl ion would tend to prevent adsorption of acid

dyes, and to favor the adsorption of basic dyes. There are, therefore, two opposite effects, the natural properties of the crystals which tend to adsorb acid dyes but not basic dyes, and the effect of alkali which forces basic dyes on to the crystal and leaches acid dyes. According to the effect which predominates, silver chloride crystals will seem to adsorb any acid or basic dye in a way that is entirely specific. The conflicting data recorded by Reinders are in this way readily explained and it becomes apparent that there is no necessary conflict between the general theory and the observed facts.

Negative ions are adsorbed on the octahedron faces of the alkali halides and barium nitrate, on the cube faces of potassium alum, and on the pyramids of sodium nitrate. The other principal faces adsorb positive ions. When for the same substance a crystal face which adsorbs negative ions is rubbed against another face which adsorbs positive ions, it is reasonable that the negative adsorbing face will become negatively charged. While cases of this kind have not generally been worked out, Vieweg¹ found that an octahedron face of sodium chloride, rubbed against a cube face of the same material, developed a negative charge. Other substances when they are tried will undoubtedly behave in the same way.

The form of a substance grown from a pure solution is governed by adsorption of molecules of the solvent upon certain crystal faces, by impoverishing the region of the particular particles needed for growth, and, as Niggli calculated, by certain fundamental properties of the crystalline substance itself. Other substances which are present in solution modify the external crystal form if they are preferentially adsorbed upon certain crystal faces, and they favor the enlargement of the faces upon which they are adsorbed. This modification of form is essentially a growth phenomenon. When urea causes common salt to grow in octahedra, it has not changed the relative stability of cube and octahedron faces. Left in contact with the mother liquor after all crystal growth has been arrested, sodium chloride octahedra will change to cubes. Foreign substances divide themselves into two groups: strongly adsorbed anions and non-electrolytes which have the same effect as anions; and strongly adsorbed cations and certain other non-electrolytes. With this clearing of the air regarding changes of crystal form where no internal rearrangement is involved, the problems presented by calcite and aragonite are greatly simplified.

Aragonite

Aragonite, like the crystals of barium, strontium, and lead carbonate which are isomorphous with it, is orthorhombic. Calcite, on the other hand, crystallizes in the rhombohedral class of the hexagonal system. The crystal structure of aragonite as determined by Huggins² on the basis of X-ray diffraction data is fundamentally different from the structure of calcite.³ A third modification of calcium carbonate is metastable under all conditions so far as known. It is hexagonal, optically positive (calcite is optically negative),

¹ Cornell University thesis, "Frictional Electricity," 36 (1924).

² Phys. Rev., (2) 19, 354 (1922).

³ Wyckoff: "The Structure of Crystals," 356 (1924).

and variously known as vaterite and μ calcium carbonate.¹ Our problem concerns itself with the reason that such metastable modifications can exist. Frequently, in its natural occurrences, aragonite is associated with barium, strontium, or lead carbonate. Since these substances form stable crystals isomorphous with aragonite, there is little doubt that much natural aragonite is stabilized by solid solution of barium, strontium or lead carbonate in the calcium carbonate crystal. But as Cornu² has pointed out, aragonite is not always associated with these elements (notably in the Erzberg mines) and certainly it is not associated with them in many laboratory preparations of the substance or in the pearly layers of the shell-fish.

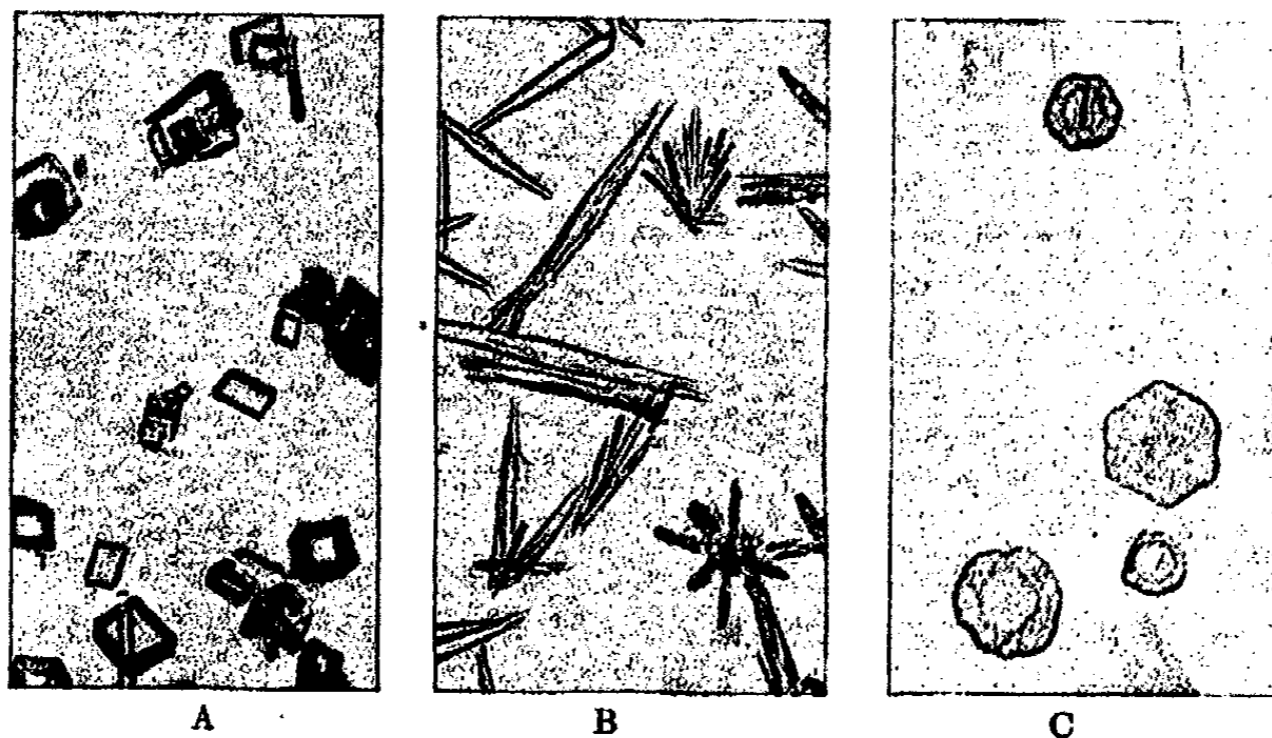


FIG. 3

- A. Calcite \times 500.
 B. Aragonite \times 500.
 C. μ Calcium carbonate \times 500.

Experiments of Rose,³ Credner,⁴ and Adler⁵ have established that aragonite separates rather than calcite when calcium carbonate is crystallized from its solution in hot water saturated with carbon dioxide or by addition of calcium chloride to a hot solution of ammonium or sodium carbonate. When the concentration of ammonium or sodium carbonate is decreased, relatively more calcite is formed at all temperatures. As L. Bourgeois⁶ and Bäckström⁷ found, the presence of urea in the hot solutions from which calcium carbonate is crystallized favors the formation of aragonite. Leitmeier⁸ is supposed to

¹ Johnston, Merwin and Williamson: *Am. J. Sci.*, 41, 473 (1916).

² *Oesterr. Z. Berg and Hüttenw.*, 45, No. 49 (1915).

³ *Pogg. Ann.*, 111, 156 (1860).

⁴ *J. prakt. Chem.*, 110, 290 (1870).

⁵ *Z. angew. Chem.*, 14, 431 (1897).

⁶ *Bull. Soc. Min.*, 6, 111 (1882); *Compt. rend.*, 103, 1088 (1886).

⁷ *J. Am. Chem. Soc.*, 47, 2432 (1925).

⁸ *Neues Jahrb. Mineral. Geol.*, 1, 49 (1910); *Neues Jahrb. Mineral. Geol. B. B.*, 40, 655 (1915).

have formed aragonite at temperatures below 20°C by employing solutions containing magnesium sulphate.¹ His conditions would certainly have given him some magnesium carbonate, yet he reports all aragonite, and his manner of testing for aragonite was probably inadequate. No chemical test can serve as a reliable criterion of an allotropic modification, and anyone who has tried to use Meigen's reaction (treating with $\text{Co}(\text{NO}_3)_2$) or Lemberg's reaction (heating with a solution of iron chloride) for aragonite will understand the precariousness of such procedure. The conditions, therefore, which favor the formation of aragonite are elevated temperature and presence in solution of an excess of carbon dioxide, alkali carbonate or urea.

It must not be forgotten that aragonite is metastable under all conditions where it has been formed: left in contact with its mother liquor it will change into calcite. Therefore, any explanation of the formation of aragonite or the still less stable μ calcium carbonate is absolutely untenable if it rests on the assumption that temperature conditions or foreign substances make calcite more soluble relatively to other forms. Any theory to account for the appearance of metastable μ calcium carbonate or aragonite must embody the idea that calcite crystals are prevented forcibly from growing.

The theory involved when we explain the formation of metastable aragonite is of tremendously broad application. All formation of monotropic modifications comes under this head; arrested transformations in the presence of colloids are potentially of the same nature; natural diamonds are formed for the same basic reasons as aragonite.

When sodium chloride crystals were grown in the presence of urea, the urea was adsorbed on the octahedron faces and retarded their perpendicular growth. There is no change of allotropic modification but only a change of external form. When H_3SbCl_6 was used instead of urea, growth normal to the octahedron face was retarded still more because adsorption was less reversible. Quinoline yellow is strongly adsorbed on potassium sulphate, and Marc² found that, with sufficient concentration of dye, potassium sulphate solution became greatly supersaturated before crystals appeared. Acid dyes will cause thallos chloride to supersaturate several hundred percent. The writer suggests, therefore, that supersaturation will always occur when there is sufficiently strong adsorption of a foreign substance upon a crystalline phase, and that supersaturation occurs because the adsorbed material dirties the surface of any crystal nucleus as soon as it appears. In this way potassium sulphate supersaturates because it has no place to start crystallizing, and in exactly the same way calcite supersaturates because adsorption dirties the surface of each new calcite nucleus. But there are two other allotropic modifications of calcium carbonate. They have different crystal structures and presumably different adsorptive properties. Aragonite crystallizes because under certain conditions it can form crystals more quickly than calcite can form crystal nuclei.

¹ Leitmeier's solution contained 0.0406 M per liter of magnesium as against only 0.100 M per liter of calcium ion.

² Z. physik. Chem., 68, 112 (1909).

Calcite adsorbs alkali carbonates, the adsorbed salts being washed out of precipitated calcium carbonate only with great difficulty.¹ It is considered, therefore, that anions, carbonate—or more probably bicarbonate-ions² and urea, which behaves like an anion, are adsorbed on the calcite nuclei, and that the high-temperature form of water favors aragonite either by being itself adsorbed upon calcite or because the low-temperature form prevents adsorption of anions. There is at present no available way of distinguishing between these two cases. It seems to be general that the high-temperature form of water favors the adsorption of anions and urea. In hot water, lower concentrations of urea or alkali are needed to cause a given development of octahedron faces on common salt, or to produce a given development of cube faces on alum. Elevated temperatures do not, however, favor formation of cube faces on barium nitrate. The influence of increased temperature is the same with calcium carbonate; urea and anions are more strongly adsorbed on calcite at the higher temperatures and favor the development of metastable modifications.

Experiments, based upon a method of Gibson, Wyckoff, and Merwin³ to prepare μ calcium carbonate, were devised to test the validity of the suggested mechanism of aragonite formation. All determinations of crystalline species were made according to the usual optical procedure. Calcium carbonate was crystallized at 60°C by adding slowly, with stirring, 0.1 M calcium chloride to a solution containing 50 gms potassium carbonate in 700 cc of water. The flask was kept in a thermostat and the precipitating agent added at the constant rate of one drop in eighteen seconds. This procedure was employed throughout this section, all preparations being made three times. Exceedingly great cleanliness is needed to prevent separation of calcite. Precipitation was continued for two and a half hours, the precipitate washed, dried with alcohol and ether, and examined microscopically. It was principally μ calcium carbonate with about 5% aragonite and a trace of calcite. When the crystallizing bath contained 20 gms of K_2CO_3 the precipitate contained principally μ $CaCO_3$ and aragonite in equal amounts and a larger amount of calcite (about 5%). When the bath contained only 10 gms of K_2CO_3 , there was virtually no μ $CaCO_3$, a large amount of aragonite and calcite, and a good proportion of indistinguishable material which was considered to be imperfectly spoiled calcite nuclei. Gibson, Wyckoff and Merwin suppose that the metastable modifications form because an excess of common ion, CO_3^{2-} , makes calcium carbonate less soluble in the solution, but if this were true an excess of the other ion, Ca^{2+} , would have the same effect. If 0.1 M K_2CO_3 is added to a solution of calcium chloride equivalent to the potassium carbonate first taken, (0.517M) nothing but calcite forms. To determine whether it was not adsorbed hydroxyl ion which peptized the calcite nuclei,

¹ Berzelius: *Jahresber.*, 23, 106 (1844); Fresenius: *Z. anal. Chem.*, 2, 44 (1863).

² Becquerel (*Compt. rend.*, 34, 573 (1852)) left gypsum in contact with a solution of potassium carbonate and in contact with a solution of potassium bicarbonate for about ten years. At the end of that time the gypsum in contact with the carbonate had been replaced by calcite and that in contact with the bicarbonate had been replaced by aragonite.

³ *Am. J. Sci.*, 10, 325 (1925).

0.1 M CaCl_2 was added to a solution containing 5 gms of $\text{Ca}(\text{OH})_2$ and 3 gms of K_2CO_3 in 700 cc of water. Nothing but calcite appeared. The evidence here presented indicates that an anion, HCO'_3 , is preferentially adsorbed on the calcite and in higher concentrations on aragonite. It is in accord with this that urea and organic anions act in the same way. Urea is known to suppress formation of calcite. When calcium carbonate is crystallized by adding 0.1 M potassium carbonate to 0.517 M calcium acetate, very few recognizable crystals are formed. The organic anion, therefore, is adsorbed on the calcite nuclei and spoils them as centers of crystal growth. If we add alcohol to a solution which would normally allow no calcite to appear, we can now predict that the alcohol will prevent adsorption of anions, and that calcite will separate. Adding 0.1 M calcium chloride at 60°C to a solution of 50 gms potassium carbonate in 700 cc of water in presence of 5 percent of alcohol gives about half calcite and half aragonite, although in absence of alcohol it is practically all μ calcium carbonate. Adsorption of anions on the calcite and to a less degree on the aragonite has peptized these forms, and allowed the appearance of another allotropic modification, a form possessing an altogether different structure. When the shell-fish prepares aragonite, he has at his command chitin and chitin-forming substances of doubtful composition, so that an exact reproduction of the mollusks' formation of aragonite is impossible. It is clear, however, that readily adsorbed organic substances having an effect identical with urea, HCO'_3 ion, and acetate ion spoil each crystal nucleus of calcite, and allow crystallization of aragonite which the mollusk wants.

The phenomenon whereby strong preferential adsorption on a stable modification allows the formation and survival of a metastable form is not unique with calcium carbonate. Many other examples have been studied, although the proper explanation has not previously been suggested. Two illustrations will suffice. Sameshima and Suzuki¹ found that when mercuric iodide was precipitated in the presence of gelatine the yellow modification was stabilized temporarily. Adsorption of gelatine or an impurity in the gelatine upon each incipient nucleus of the red form prevents further growth and tends to preserve the unstable form in a metastable condition. Cohen² states that "electrolysis of an antimony solution produces the monotropic, metastable, β modification of the metal . . . β antimony tends to change to the stable α form at all temperatures." Cohen has found that the solid metal contains certain amounts of antimony trichloride, as he believes, in solid solution. On the other hand, since the solid solution of salts in metal is exceedingly rare, probably impossible, it is more likely that antimony trichloride is adsorbed upon the small amount of α form that is present and that it stabilizes the β form by stopping the α form from growing. This mechanism is exactly analogous to the stabilization of aragonite by strong preferential adsorption.

Spangenberg³ supposed that a complex, hydrated sodium-and-urea cation was the cause of the octahedron faces upon sodium chloride, but he gave no

¹ Bull. Chem. Soc. Japan, 1, 81 (1926).

² "Physico-Chemical Metamorphosis," 37 (1926).

³ Z. Krist., 59, 375 (1924).

good reason why such a cation should have that effect. In every other case studied, urea has the same influence as readily adsorbed anions and its influence is diminished by the same factors that counteract the effect of anions. To account for the effect of urea in all these cases Spangenberg would have to postulate for every substance a new complex which controlled crystal form in the same mysterious fashion. Simpler and capable of indirect proof is the suggestion that urea is always preferentially adsorbed on the same crystal faces as readily adsorbed anions and that the consequent decrease of growth perpendicular to those faces favors their enlargement. We cannot expect that there will always be as excellent accordance in the adsorption of similar substances as has been encountered in this work. All work upon adsorption shows that, while certain ions are usually more strongly adsorbed than others, no rigid sequence will hold in all cases. There are, however, fewer specific variables when a crystal surface is the solid adsorbent. The crystal surface is at least a plane surface and no complications arising from the gross structure of the adsorbing surface prevent the formation of exact laws of adsorption.

Summary

1. All crystalline substances adsorb from their mother liquor ions of electrolytes and molecules of solvent and dissolved non-electrolytes.
2. Adsorption upon a crystal face retards growth normal to the surface and favors enlargement of the form.
3. When a cation is preferentially adsorbed upon one face species of a crystal, anions are preferentially adsorbed upon the other principal crystal faces.
4. The non-electrolytes, urea, glycocholl, and mercuric chloride are adsorbed upon the same crystal faces as readily adsorbed anions.
5. Alcohol tends to prevent adsorption of anions.
6. Adsorption of anions upon the instable octahedron faces of the alkali halides, the cube faces of the alums, and upon the end forms of sodium nitrate favor their enlargement. Adsorption of cations upon the cube faces of barium nitrate and upon the side forms of sodium nitrate increase the size of these faces.
7. Sufficiently strong preferential adsorption upon an allotropic modification will spoil each crystal nucleus as a center for crystal growth, and tend to obstruct the modification. This allows an instable allotropic modification to be stabilized temporarily.
8. Aragonite and μ calcium carbonate are enabled to exist because bicarbonate ion, acetate ion, urea, the high-temperature form of water, and organic material in the shells of mollusks are preferentially adsorbed on calcite and prevent growth of calcite crystals.

This problem was suggested by Professor W. D. Bancroft, whose advice has at all times been invaluable.

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ACTIVITY COEFFICIENTS AND MASS-ACTION LAW IN ELECTROLYTES¹

BY L. ONSAGER

In two recent papers,² F. G. Soper claims that in considering chemical interaction in dilute solutions of electrolytes, the activity coefficients should be taken according to the formula:

$$\ln f_i = - z_i^2 \kappa \frac{e^2}{3 D k T} \quad (1)$$

He thus rejects the original formula given by Debye and Hückel,³ which is:

$$\ln f_i = - z_i^2 \kappa \frac{e^2}{2 D k T}; \quad (2)$$

z = valence; e = charge of an electron; D = dielectric constant; k = Boltzmann's constant; T = abs. temp.; κ = mean inverse radius of the ionic atmosphere, given by the equation:

$$\kappa = \frac{4\pi e^2}{D k T} \sum_{i=1}^s n_i z_i^2$$

when n_i means the number of ions of the kind i present in 1 cm³ of the solution, and the sum is taken over all kinds of ions present in the solution.

The value found by Soper for $\log f$ is just $\frac{2}{3}$ of that found by Debye and Hückel. Of course, both the expressions (1) and (2) cannot be right at the same time.

I am going to show, that Soper's formula (1) is wrong, and depends upon an erroneous deduction from some of the results given by Debye and Hückel.

In his first paper, Soper argues as follows: "The total free electric energy of a solution of n ions, found by charging them reversibly⁴ is $\frac{1}{2} n z e \psi$, where ψ is the potential at one of these ions due to the surrounding "ion atmosphere." Part of this electrical free energy resides in the medium, but change in the partial free electrical energy of the ions is attended simultaneously by a change in the electrical free energy of the medium. The potential energy possessed by a pair of ions with respect to their combination will be the difference of the total work done in charging the ions A and B and that done in charging the complex formed by collision of A and B. If the ions have charges z_A and z_B , the complex will have the charge $z_A + z_B$ and the potential energy of A and B will be given by:

$$\frac{1}{2} e \{ z_A \psi_A + z_B \psi_B - (z_A + z_B) \psi_{A,B} \} \quad (3)$$

¹ Contribution from the Johns Hopkins University, Baltimore, Md.

² J. Phys. Chem., 31, 1790 (1927); 32, 67 (1928).

³ Physik. Z., 24, 185 (1923).

⁴ Debye: Physik. Z., 25, 97 (1924).

The potential ψ_i , at an ion i due to its surrounding ionic atmosphere is given by:

$$\psi_i = -\frac{z_i e \kappa}{D} = -\frac{z_i e}{D} \sqrt{\frac{4\pi \sum_j n_j z_j^2}{D k T}} = -\frac{z_i}{D} \sqrt{\frac{8\pi e^3 N \mu}{10^3 D k T}} \quad (4)$$

where n_i is the number of ions of the i 'th kind per cc. in the solution, e the charge on an univalent ion, N the Avagadro number and k the gas constant per molecule."

In citing the above, a couple of obvious misprints in the formulae (3) and (4) have been corrected. These formulae were not numbered in Soper's paper.

Soper says "the total potential energy possessed by an ion in virtue of its charge is $\frac{1}{2} z e \psi$." He means the potential energy with respect to the surrounding ions; however, he goes too far in treating the energy as a particular property of the ion.

The influence of the electrical forces between the ions, at equilibrium, is given by the change δW in the total free electrical energy W involved by a small displacement of the equilibrium. Let this displacement involve changes $\delta N_o, \delta N_1, \dots, \delta N_s$ in the total numbers N_o, N_1, \dots, N_s of the molecules and ions of each kind $o, 1, \dots, s$ present (the index o indicates the solvent). The change:

$$\delta W = \sum_{i=0}^s \frac{\partial W}{\partial N_i} \delta N_i$$

is obviously completely given when the partial free energy:

$$\bar{w}_i = \left(\frac{\partial W}{\partial N_i} \right)_{p, T, N_o, N_1, \dots, N_{i-1}, N_{i+1}, \dots, N_s}$$

is given for each kind i of molecules (ions) entering the reaction: because, for the others, $\delta N_i = 0$. Now, the change in the free electrical energy W involved by introducing an ion¹ is given (practically) by the work necessary to charge it in the solution. However, the sum of the partial free electric energies of the ions is not equal to the work required to charge them all either simultaneously or successively, that is, to the total free electric energy. And, accordingly, the partial free energies cannot be obtained simply by distributing the total free electric energy between the ions even in the most reasonable manner, because the sum cannot possibly fit, at any rate, not as long as the square root law holds. The partial free energies \bar{w}_i are obtained by derivation of the total free energy, as shown above.

The difference² between the work necessary for charging the ion in the electrolyte and that necessary for charging it in the neutral solvent amounts to:

¹ In reality, we cannot determine the partial free energy of a single ion, but only the sum of the partial free energies of such a combination of ions for which the sum of the charges is zero, or differences between the partial free energies for ions of the same charge or combinations of the same total charge.

² $\bar{w}_i = \frac{1}{2} e_i z_i \psi_i$ as long as ψ_i is proportional to z_i , which is true for small concentrations.

In general we must put: $\bar{w}_i = \int_{\lambda=0}^{\lambda=z_i} \psi(\lambda e) d(\lambda e)$ considering the potential as a function of the charge.

$$\bar{w}_i = \frac{1}{2} e z_i \psi_i = - \frac{e^2 z_i^2 \kappa}{2 D} \quad (5)$$

and not $\frac{1}{2} e z_i \psi_i$. Thus the partial free electrical energy of the ion is $\frac{1}{2} e z_i \psi_i$ (+ a constant which does not vary with the concentration). However, the total free electrical energy of the electrolyte is only

$$W = \frac{1}{2} \sum_{i=1}^n N_i z_i e \psi_i = - \frac{e^2 \kappa}{3 D} \sum_{i=1}^n N_i z_i^2 \quad (6)$$

when $N_1 \dots N_1 \dots N_n$ mean the total numbers of the different kinds of ions present. This is easily seen by considering the process of charging the ions one by one. The work of charging the first ions will not at all differ from that required to charge them in pure solvent. When so many ions are charged, that the ionic strength has increased to a fraction λ of its final value, the work of charging an ion of the i 'th kind will be:

$$- \frac{e^2 z_i^2}{2 D} \kappa' = - \frac{e^2 z_i^2}{2 D} \kappa \sqrt{\lambda}$$

as the mean radius r/κ' of the ionic atmosphere at that moment will amount to $r/\sqrt{\lambda}$ times its final value r/κ which is not reached until all ions are charged.

Let us charge the ions in such an order, that we have approximately equal fractions of the ions of each kind charged at the same time. Thus, at a certain stage of the process, numbers $\lambda N_1, \dots, \lambda N_1 \dots \lambda N_n$ of each kind are charged. The work needed for charging further $N_1 d\lambda \dots N_1 d\lambda \dots N_n d\lambda$ ions of each kind will be:

$$dW = \sum_{i=1}^n N_i d\lambda \left(- \frac{e^2 z_i^2}{2 D} \kappa \sqrt{\lambda} \right) = - \frac{e^2 \kappa}{2 D} \sum_{i=1}^n N_i z_i^2 \sqrt{\lambda} d\lambda$$

the work needed for charging these ions separately in pure solvent being subtracted. The total work is found by summing up all steps. This gives us:

$$W = \int_{\lambda=0}^{\lambda=1} dW = - \frac{e^2 \kappa}{2 D} \sum_{i=1}^n N_i z_i^2 \int_{\lambda=0}^{\lambda=1} \sqrt{\lambda} d\lambda = - \frac{e^2 \kappa}{3 D} \sum_{i=1}^n N_i z_i^2 \quad (6)$$

The total free electrical energy W can be considered as a function of the pressure p , the temperature T , the numbers $N_1, N_2 \dots N_n$ of the different kinds of ions, and the number N_o of the molecules of solvent. In these variables, \bar{w}_i must be equal to $\frac{\partial W}{\partial N_i}$; because the change in W involved by

introducing one more ion of the i 'th kind is $\frac{\partial W}{\partial N_i} \delta N_i = \frac{\partial W}{\partial N} \cdot i$, and this

change in W must equal the work \bar{w}_i required to carry out this change of the system. Now, this is easily controlled by deriving the expression for W given by (6). In carrying out this derivation, we must remember that κ is a function of the numbers N_i :

$$\kappa^2 = \frac{4\pi}{DkT} \sum_{i=1}^s N_i z_i^2 = \frac{4\pi}{DkT} \frac{\sum_{i=1}^s N_i z_i^2}{V};$$

here, V means the total volume of the system. Owing to the fact that we have to deal with a dilute solution of small compressibility, we have until now neglected the change in the volume involved by introducing and charging the ions. It may be shown that this approximation involves but a small error, and it has nothing to do with those principal features of the theory which we are discussing here. Therefore, we will assume that the volume is given by the solvent molecules alone:

$$V = N_o v_o;$$

v_o meaning volume per molecule of the solvent. Thus we have:

$$\kappa^2 = \frac{4\pi}{DkT} \frac{\sum_{i=1}^s N_i z_i^2}{N_o v_o} \quad (7)$$

$$\frac{\partial \kappa}{\partial N_i} = \kappa \frac{z_i^2}{2 \sum_{j=1}^s N_j z_j^2} \quad (i = 1, 2, \dots, s)$$

Now the derivation of W gives:

$$\begin{aligned} \frac{\partial W}{\partial N_i} &= \frac{\partial}{\partial N_i} \left(-\frac{e^2 \kappa}{3D} \sum_{j=1}^s N_j z_j^2 \right) \\ &= -\frac{e^2 \kappa}{3D} z_i^2 - \frac{e^2}{3D} \kappa \frac{z_i^2}{2 \sum_{j=1}^s N_j z_j^2} \sum_{j=1}^s N_j z_j^2 \\ &= -\frac{e^2 \kappa}{2D} z_i^2 = \bar{w}_i \end{aligned} \quad (8)$$

Now, according to (6) and (7) the free electrical energy is an extensive property of the system. Every such function obeys a relation of the form:

$$W = \sum_{i=0}^s N_i \bar{w}_i = \sum_{i=0}^s N_i \frac{\partial W}{\partial N_i} \quad (9)$$

Comparing this with (8) and (6), it is easily seen that $\bar{w}_o = \frac{\partial W}{\partial N_o}$ cannot be

zero. In this respect, therefore, one may say that part of the free electric energy "resides in the medium." \bar{w}_o is easily obtained:

$$\frac{\partial W}{\partial N_o} = -\frac{e^2}{3D} \frac{\partial \kappa}{\partial N_o} \sum_{i=1}^s N_i z_i^2$$

According to (7):

$$\frac{\partial \kappa}{\partial N_o} = -\frac{\kappa}{2N_o}$$

Thus:

$$\bar{w}_0 = \frac{\partial W}{dN_0} = \frac{e^2 \kappa}{6 D N_0} \sum_{i=1}^s N_i z_i^2 = - \frac{W}{2 N_0} \quad (10)$$

Now it is easy to see that (9) is fulfilled. According to (8) and (6):

$$\sum_{i=1}^s N_i \bar{w}_i = \sum_{i=1}^s N_i \frac{\partial W}{dN_i} = - \frac{e^2 \kappa}{2 D} \sum_{i=1}^s N_i z_i^2 = \frac{3}{2} W$$

Thus, making use of (10):

$$\sum_{i=0}^s N_i \bar{w}_i = N_0 \bar{w}_0 + \sum_{i=1}^s N_i \bar{w}_i = - \frac{1}{2} W + \frac{3}{2} W = W$$

Now; Soper says: "Part of this electrical energy resides in the medium, but change in the partial free electrical energy is attended simultaneously by a change in the electrical free energy of the medium." The meaning seems to be that a change in the number of ions of the i 'th kind alters the partial free energy of the medium. This is true, but the partial free energies of all kinds of molecules, ions as well as solvent, are changed.

When we derive:

$$\frac{\partial W}{dN_i} = \frac{\partial}{dN_i} \sum_{j=0}^s N_j \bar{w}_j = \bar{w}_i + \sum_{j=0}^s N_j \frac{\partial \bar{w}_j}{dN_i},$$

it follows from the definition:

$$= \bar{w}_i \frac{\partial W}{dN_i},$$

that:

$$\sum_{j=0}^s N_j \frac{\partial \bar{w}_j}{dN_i} = 0$$

so that all the changes in the partial free electrical energies just compensate each other.

This may be enough to show that Soper's results depend upon his misunderstanding of the term "partial free energy," and that the theory of Debye and Hückel is satisfactory in all points attacked by him, as far as the deductions are concerned.

Soper tests his own formulae on experiments performed by various authors on reaction velocity. He finds them to fit better than the formulae of Debye and Hückel, applied to reaction velocity by Brönsted. However, these experiments are made at so high concentrations that large deviations

from the limiting formulae given by Debye and Hückel must be expected. At such high concentrations, a square root formula may fit for interpolation over a certain range, just as a tangent fits a curve. But it should be emphasized, that the only sound application of the square root formula is to use it with the theoretical coefficient as an asymptotic formula for small concentrations. Univalent binary electrolytes in water may fit the limiting formulae fairly well up to an ionic strength of 0.01; for others, the limit must be taken still lower.

Summary: The considerations of F. G. Soper, which lead to other limiting formulae for the activity coefficients of electrolytes than those given by Debye and Hückel, were analyzed and shown to be erroneous. The fact that Soper's formulae agree better with the experiments considered by him is attributed to his applying the limiting square root formulae at too high concentrations.

THE VELOCITY OF ESTERIFICATION OF AMIDES IN ALCOHOL

BY H. AUSTIN TAYLOR AND THOMAS W. DAVIS¹

In 1863 Berend² noted that formamide and its homologues react with alcohol in the presence of hydrochloric acid to yield fatty esters. Later, Bonz³ showed that amides can be esterified by heating with alcohol, although frequently the salt of the corresponding amine is also formed. Reid⁴ in this manner was able to isolate benzoethylamide from benzamide and alcohol. A kinetic study of the rate of esterification was made by Reid⁵ of three aromatic amides in nearly dry alcohol at 50°C. The reactions, carried out in sealed tubes, were followed by determining the amount of ammonium salt formed. The acid concentrations were high, from 1 M to 3 M, and no account was taken of the interaction of this with the alcohol. The data obtained consequently were necessarily rough, and from this point of view alone a more detailed study is desirable.

Since this reaction does not involve water in either the reactants or resultants, it constitutes one of a class of very few members which may be investigated to determine the disturbing effect of water on reaction rate, a problem which has become of importance due to the recent controversy concerning the nature of the catalyst in homogeneous acid catalysis. Lapworth⁶ appears to have been the first to suggest that the dry hydrogen ion is the active catalyst and on that basis arrived at results which were in agreement with those of Goldschmidt⁷ who assumed the alcoholated hydrogen ion to be the catalyst. More recently Lapworth's view has been championed by Rice⁸ who showed that the temperature coefficient of many reactions catalysed by strong acids is the same, independent of added neutral salt. This observation was taken to indicate that the temperature effect is solely due to a change in the H⁺ ion concentration.

Brönsted⁹ on the other hand believes the hydrogen ion to exist in aqueous solution chiefly as the oxonium ion H₃O⁺, the actual concentration of free hydrogen ions being very small. In solvents other than water, other solvates presumably must be considered. Brönsted's view is substantiated somewhat by the calculation of Fajans¹⁰ of 262,000 calories per mole being the heat of

¹ Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

² Ann., 128, 337 (1863).

³ Z. physik. Chem., 2, 883 (1888).

⁴ Am. Chem. J., 45, 38 (1911).

⁵ Am. Chem. J., 41, 483 (1909).

⁶ J. Chem. Soc., 93, 2163, 2187 (1908); 97, 19 (1910); 101, 2249 (1912); 107, 857 (1915).

⁷ Ber., 28, 3218 (1895); Z. Electrochemie, 12, 432 (1906). See also Millar: Z. physik. Chem., 85, 129 (1913).

⁸ J. Am. Chem. Soc., 45, 2808 (1923).

⁹ J. Am. Chem. Soc., 49, 2554 (1927).

¹⁰ Ber. deutsch. physik. Ges., 21, 709 (1919).

hydration of gaseous hydrogen ions, a figure which must necessarily render the number of free ions in water extremely small. Whether the actual figure may be accepted seems doubtful since it is from the physical viewpoint the energy necessary to polarise an indefinite group of water molecules by electrostatic forces. The order of magnitude nevertheless must be correct and the above result therefore essentially the same whatever the real value. On the basis of the oxonium ion being the catalyst Brönsted has shown that the results of previous investigators have a simple explanation. Despite this simplicity however, no explanation of the mechanism of catalysis is forthcoming.

Kastle¹ appears to have been the first to favor the intermediate compound theory of homogeneous catalysis, a theory substantiated for example in the case of ether formation where the compound may be isolated. The researches of Kendall² too have proved the existence of acid-ester complexes, the stronger the acid and the more basic the organic radicals of the ester, the more extensive is compound formation. The intermediate compound theory, coupled with the more recent activity views, has received considerable attention of late from Brönsted³ and suffice to say, the resulting interpretations, particularly of neutral salt action in general, warrant the closest consideration.

It appears then that whatever the catalyst, a mechanism is still required. Furthermore it might be expected that the effect of water would be of prime importance. Of the reactions studied in non-aqueous solvents and in presence of traces of water the majority show an inhibiting effect of water on the velocity. The work of Taylor and Close⁴ seems to be an exception. The velocity of lactone formation from hydroxy acids is extremely small in dry ether solutions but rises rapidly as water is added in increasing amounts. Even these results are in contrast with the behavior of the same reaction in alcohol, and alcohol-water solutions where Kailan and Neumann⁵ found a depressing effect of water similar to that observed in the velocity of esterifications and in the decomposition of diazo-esters in alcoholic solutions.

Such varied phenomena do not seem to admit of a simple explanation on the basis either of free hydrogen ion or the oxonium ion without consideration of the effect of water and possibly also alcohol or ether on the substrate itself. It is obvious that one must look to the substrate and its condition in the various solvents to decide whether the reaction is to be accelerated, unchanged, or retarded by water or in fact accelerated for one range and retarded for another or vice-versa. Such would seem to be the possibilities that could arise. It was with such thoughts in mind that the above reaction was studied.

¹ Am. Chem. J., 19, 894 (1897).

² Inter alia, J. Am. Chem. Soc., 38, 1712 (1916); 43, 1826 (1921); J. Chem. Soc., 127, 1789 (1925).

³ Z. physik. Chem., 102, 169 (1922).

⁴ J. Phys. Chem., 29, 1085 (1925).

⁵ Z. physik. Chem., 93, 111 (1920); 101, 63 (1922).

Experimental

1. Preparation of Materials.

a. Alcohol. The literature contains a large number of articles on the preparation of dry alcohol. MacArdle¹ has summed up the methods in excellent fashion. The method finally adopted was Winkler's, using calcium. Metallic calcium, kept under kerosene, was washed with carbon tetrachloride to remove the oil, then rinsed several times with alcohol and added to the alcohol to be dried in the proportion of 20 g. per liter of alcohol containing an average of 0.25 per cent of water. The calcium was allowed to react slowly in the cold for a day or two, after which the alcohol was distilled through a fractionating column. Although boiling over completely within a range of a tenth of a degree, a small portion of the initial and final distillate was rejected. Out of fifteen instances of the above only two required a second treatment with calcium. The anhydrous ethanol was kept in a bottle protected from atmospheric moisture by a tube of phosphoric anhydride.

There appears to be a general disagreement regarding the best method of determining moisture in alcohol. The density determination seemed most satisfactory and gave results comparable with the accepted figures of the Bureau of Standards. To this end a 25 cc. specific gravity bottle was used. An accuracy of one part in 8000 corresponding to a water content of one part in 7000 or 0.015 per cent is easily attainable.

The rate at which alcohol absorbs moisture is a matter for discussion. One experiment tried, in which 50 ccs. of absolute alcohol in a graduate 25 mm. \times 130 mm. were left open to the air in the laboratory (26°C and 761.2 mm. pressure) for 22 minutes showed no change in density. Alcohol however, poured through the air or kept in cork-stoppered bottles for three or four weeks was found to take up 0.03-0.08 per cent water.

Alcohol showing more than 0.02 per cent water was not used in the experiments requiring absolute material. Moist alcohol was obtained by adding water or 95% alcohol to the anhydrous or nearly anhydrous material, the actual content being determined from the density.

b. Formamide. Inconsistent melting points for formamide are to be found in the literature, a value of 2.2°C being apparently the most reliable. Of the varied methods of purification, that of Merry and Turner², a fractional distillation under reduced pressure, gave the most satisfactory results. Kahlbaum's formamide melting at -5.5°C or Eastman's melting at -4.5°C was allowed to stand over anhydrous sodium sulphate for several days, after which it was distilled (B.P. 110-135°C at 30-45 mm. pressure). The first distillation was accompanied by an odor of ammonia which disappeared after two distillations. For seven successive fractionations, a quantity of white crystals condensed in the receiver. These were presumably ammonium formate and dissolved readily in the first few drops of liquid coming over. Fifteen distillations finally yielded a sample melting at 2.20°C and as judged from the

¹ "Solvents in Organic Chemistry", (1921).

² J. Chem. Soc., 97, 2069 (1910); English and Turner: 105, 1656 (1914).

melting point curve was practically pure. The figure agrees with that of Brann¹, 2.25°C. Although the original substance was quite acid to litmus, the final product was slightly alkaline and quite odorless. Values of the density, 1.1349 at 19°C, 1.1339 at 20.1°C, and 1.1301 at 24.6°C are in agreement with data given by Beilstein.

c. Acetamide. Three recrystallisations of Baker's analyzed acetamide from acetone or from chloroform yielded a pure product without odor, melting at 79°C.

d. Propionamide. Eastman's propionamide was recrystallised three times as for acetamide, dried at 75°C, crushed and kept over P₂O₅. The strong acid odor of the original was entirely removed in the process, the final product melting at 79.5°C.

e. Benzamide. Commercial benzamide purified by recrystallisation from hot water gave a pure product melting at 127-127.5°C.

f. Alcoholic HCl. Hydrogen chloride from hydrochloric acid and sulphuric acid was absorbed in absolute alcohol in an apparatus so arranged that either alcohol or acid could be added without exposure to the atmosphere. No attempt was made to maintain the acid concentration constant in all the experiments, but by dilution the normality was generally kept between 0.2 and 0.6 N. Solutions were used as soon after preparation as possible to avoid the disturbing effect from the interaction of alcohol and acid.

g. Baryta. N/10 baryta was used as alkali in the titrations since being a weaker base than sodium or potassium hydroxides it was less apt to cause hydrolysis during titration. As indicator methyl orange was used except where otherwise stated, the usual precautions being taken to prevent action of carbon dioxide on the solution.

h. Other materials. Ammonium formate, ammonium chloride and bromide, and ethyl formate were purified in the usual manner from Kahlbaum material.

2. Method of Measurement.

In the first experiments with benzamide at 45°C a weighed quantity of the amide was dissolved in alcohol in a volumetric flask at 45°C leaving room for addition of 6N HCl in alcohol. A suitable amount of acid being added the flask was filled to the mark, shaken, returned to the thermostat and the time noted. Samples were pipetted out and titrated. At convenient intervals thereafter samples were removed, run into ice water to stop the reaction and titrated almost to neutrality. In order to fix the end point however the solution had to be allowed to attain room temperature on account of the sensitivity of the indicator to temperature fluctuations. An attempt to reduce losses of alcohol by evaporation by fixing a pipette permanently to the reaction flask did not prove satisfactory and was discarded in later runs.

With formamide at 25°C the flask was filled sufficiently beyond the mark to allow removal of two samples of the alcoholic HCl for titration. Further excess was then removed until the solution stood at the mark on the flask.

¹ J. Am. Chem. Soc., 40, 793 (1918).

Formamide was then run in from a pipette or better a weighed amount added from a small weighing tube, the tube and stopper finally being dropped in also. The solution was shaken and returned to the thermostat, the whole operation requiring less than a minute. The initial time, that is, the time of mixing could be noted with an accuracy of 10-15 seconds. The initial titer was corrected for the amide added. From time to time samples were withdrawn with an open pipette and run into a measured deficiency of baryta and rapidly titrated to avoid further reaction and hydrolysis of the ethyl formate. Manning¹ has observed that the hydrolysis of ethyl formate is catalysed by baryta. The end points of these titrations were not sharp. The heat of reaction is so high that the temperature was maintained about 0.25°C too high over the measured period. The main source of error in the experiment was in the time, an error of half a minute in the time corresponding to 0.05 cc. in the titer. The percentage error in the velocity constant was the same as the percentage error in the time.

With acetamide and propionamide, weighed amounts of the amide were added directly to the alcoholic hydrogen chloride solution at the desired temperature. The rate of solution of the amides is sufficiently rapid to warrant such a procedure. The speed of esterification with these substances renders the main error in the measurements, the error in the titration, an error of 0.01 cc. in the titer corresponding only to twenty minutes in the time. Check titrations therefore were run in every case.

The usual bimolecular constant, representing the reaction between a molecule of amide and a molecule of acid was calculated in each case.

$$k = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

where t = time in minutes
 a = initial acid concentration in moles per liter
 b = initial amide concentration in moles per liter
 $a-x, b-x$ = concentrations after t minutes

Since as the esterification proceeds ammonium chloride is formed, the alcoholic solution eventually became saturated and the salt precipitated. The observed effect of this on the velocity constant was small, though tests were made using solutions containing ammonium chloride or bromide initially, to discover the effect of added neutral salt.

Experimental Results

The results of the first experiments using benzamide at 45°C though quite inconsistent among themselves indicated a bimolecular constant of the order 1×10^{-4} . The inconsistencies are due doubtless to the error caused by loss of alcohol by evaporation at this temperature and also that alcohol reacts with hydrogen chloride at 45°C giving a bimolecular constant of the order 1×10^{-6} . The actual results therefore need not be given.

¹ J. Chem. Soc., 119, 2079 (1921).

Formamide at 25°C gave a bimolecular constant of the order 5×10^{-2} but the constant seems approximately proportional to the amide concentration. A trimolecular constant when calculated however was no more constant than the bimolecular and the results therefore list k' , the bimolecular constant divided by amide concentration. The results nevertheless are not entirely satisfactory. Six experiments with solutions initially saturated with ammonium chloride and acid concentrations of about 0.6 N and amide from 0.2 to 0.45 N gave a mean value of $k' = 1.31 \pm 0.07$. Two mixtures containing 0.2 N NH_4Br gave a mean value of 1.75. One system containing 0.45 N amide and 0.28 N acid yielded $k' = 1.42$. To test whether some impurity in the formamide was affecting the velocity a run was made using 200 ccs. of solution. The value of k' was 1.22. The following day this same solution was again used, more amide being added and the velocity determined. A value of $k' = 2.01$ was found. The actual figures may be considerably in error since great difficulty was experienced in the determination of end points. Nevertheless a very definite acceleration in reaction velocity is to be seen. If the bimolecular constant be divided by the sum of the amide concentrations of the two experiments a value of $k' = 1.04$ is obtained. This would seem to indicate the presence of an impurity, possibly a tautomer of the formamide (the existence of which is well known) which slowly changes into a reactive form. The presence of an impurity is less likely since the purer the amide the higher was the constant obtained. Two cases of the constants obtained may be quoted as examples, the first with amide in excess, the second with acid in excess.

TABLE I

| Experiment 31 | | | Experiment 101 | | |
|------------------------------------|-------|-----------------|-----------------------------------------------------------|--------------|------|
| HCl = 0.2812 N Amide = 0.4488 N | | | HCl = 0.4389 H ₂ O = 0.0% Amide = 0.2457 | | |
| t | Titer | $k \times 10^3$ | t | Titer | k |
| 0 min. | 16.09 | — | 0 min. | 23.47 | — |
| 30.25 | 8.16 | 7.34 | 33 | 17.26 | 5.21 |
| 45.5 | 5.89 | 6.54 | 39.5 | 16.69 | 5.39 |
| 60.25 | 4.60 | 6.52 | 48 | 16.21 | 4.47 |
| 83 | 2.90 | 7.53 | 56 | 14.92 | 5.58 |
| 237 | 0.06 | 11.16 | 65 | 14.40 | 5.56 |
| — | 0.07 | 5.43 | 1477 | 11.66 | |
| | | | 2826 | 11.18 | |
| | | | 4221 | 11.32 | |
| | | | 5673 | 11.48 | |
| | | | 6810 | 11.31 | |
| | | | | 10.33 Theor. | |

The titrations after the first six results in the latter did not yield sharp end points and the values of k were not calculated.

The results with pure formamide (M.P. 2.20%) are summarised in Table II. The constants are the averages only of 3, 4 or 5 determinations taken from 30 to 100 minutes after the start. All solutions were saturated with NH_4Cl at the start. Others noted contained also NH_4Br . It should be noted here that the reference values of the solubilities of NH_4Cl , 0.67 g. per 100 g. solution at 25°C, and NH_4Br , 3.2 g. per 100 g. solution seem considerably too high. In dry alcohol containing 0.43 and 0.31 moles of acid per liter, solubilities for NH_4Cl were found of 0.583 and 0.586 respectively. In 0.12 N HCl in alcohol containing 0.48 per cent of water, the solubility was 0.619 per 100 g. solution.

TABLE II

| Expt. | % H_2O | N acid | N amide | NH_4Br | $k' \times 10^{-1}$ |
|-------|------------------------|--------|---------|------------------------|---------------------|
| 65 | 0.0 | 0.5165 | 0.2178 | — | 1.67 |
| 60 | 0.0 | 0.3913 | 0.2079 | 0.018 | 2.47 |
| 49 | 0.025 | 0.4847 | 0.2451 | — | 1.91 |
| 101 | 0.05 | 0.4389 | 0.2457 | — | 2.16 |
| 67 | 0.10 | 0.4190 | 0.2488 | — | 2.15 |
| 70 | 0.10 | 0.4472 | 0.2158 | 0.026 | 2.24 |
| 74 | 0.10 | 0.3560 | 0.2256 | 0.026 | 2.54 |
| 87 | 0.48 | 0.3313 | 0.2085 | — | 2.45 |
| 91 | 1.22 | 0.5022 | 0.2590 | — | 1.17 |
| 94 | 1.22 | 0.4982 | 0.2456 | — | 1.24 |
| 98 | 2.75 | 0.6117 | 0.2457 | — | 0.85 |

The results would at first sight suggest a maximum effect of water in the neighborhood of 0.5 per cent water. Solutions containing 1.22 per cent of water gave evidence however that an appreciable amount of hydrolysis was taking place. To test this definitely ethyl formate hydrolysis was studied in two cases, one in 97.1 per cent alcohol by weight and one in 92.42 per cent. The data are given in Table III.

TABLE III

| Experiment 110 | | Experiment 117 | |
|------------------|-------------------------------|------------------|------------------------------|
| Acid = 0.4409 N | $\text{H}_2\text{O} = 7.58\%$ | Acid = 0.3653 N | $\text{H}_2\text{O} = 2.9\%$ |
| Ester = 0.2404 N | | Ester = 0.2462 N | |
| t | Titer | t | Titer |
| 0 min. | 23.58 ccs. | 0 min. | 19.42 ccs. |
| 35.5 | 28.34 | 41 | 24.56 |
| 44.5 | 29.60 | 56 | 25.02 |
| 53 | 30.38 | 72 | 25.75 |
| 61 | 30.29 | 93 | 26.75 |
| 69 | 30.28 | 1340 | 26.70 |

Cresol red which changes in a pH range of 7.2-8.8 was used as indicator, so that the titrations included free formic acid. It is certain therefore that in solutions containing as little as 3 per cent water, ethyl formate is hydrolysed

quite rapidly and consequently the esterification constant in 1.22 and higher percentages of water is too low due to hydrolysis. The hydrolysis equilibrium must lie far on the alcohol-acid side.

The experiments dealing with the temperature disturbance in the formamide reaction are given in Table IV. In each case 100 ccs. of alcoholic HCl about 0.45 N was allowed to attain the temperature of the thermostat ($25 \pm 0.02^\circ\text{C}$), 1.1 g. of formamide was then added, the solution shaken and a thermometer inserted and read at minute intervals. For brevity only a few values are given, though the observed temperatures were the same throughout the time shown, demonstrating a large heat of reaction.

TABLE IV

| Time | I | II | Time | I | II |
|--------|---------|---------|---------|---------|---------|
| 0 min. | 25.08°C | 25.09°C | 45 min. | 25.23°C | 25.26°C |
| 5 | 25.36 | 25.40 | 70 | 25.18 | 25.17 |
| 10 | 25.36 | 25.36 | 122 | — | 25.17 |
| 15 | — | 25.31 | 760 | — | 25.07 |
| 20 | 25.33 | 25.35 | | | |

Since ammonium formate might possibly be present as an impurity, and further since it is one of the few readily available neutral salts possessing a reasonable solubility in alcohol, experiments were tried using mixtures of formamide and ammonium formate. The resulting constants being very much larger than for formamide alone it was suspected that the formate also was reacting with alcohol, the results of a test of which are given in Table V. The figures for ammonium acetate, corrected approximately for the reaction between HCl and alcohol are given for comparison.

TABLE V

| Experiment 62 | | | Experiment 66 | | |
|------------------------------------------------------------------------|------------|----------|-----------------------------------------------------------------------------------|---------------|--------------------|
| Acid = 0.3603 N $\text{NH}_4\text{O}_2\text{CH} = 0.0429 \text{ N}$ | | | Acid = 0.3652 N $\text{NH}_4\text{O}_2\text{C}_2\text{H}_5 = 0.0259 \text{ N}$ | | |
| t | Titer | k | t | Titer (corr.) | k |
| 0 min. | 21.29 ccs. | — | 0 min. | 21.55 ccs. | — |
| 53.5 | 19.44 | 0.0720 | 1270 | 21.52 | — |
| 72 | 19.43 | 0.0534 | 2800 | 21.55 | — |
| 88 | 19.40 | 0.0459 | 5800 | 21.51 | — |
| 1521 | 18.94 | (0.0052) | 8575 | 21.47 | 2×10^{-5} |

The ammonium formate therefore is reacting almost as fast as the formamide. With ammonium acetate however this disturbance is not to be expected. The rapidity with which formamide reacts precludes the necessity of correcting for the alcohol-HCl reaction although it suffers as has been seen other greater difficulties. With acetamide and propionamide the esterification is much slower and it is necessary to see exactly how important is the alcohol-HCl reaction. Table VI gives the results of a typical test. Data are also added to show how this reaction affects a typical acetamide esterification reaction.

TABLE VI

| Experiment 41a Alcoholic HCl = 0.7796 N | | Experiment 41b HCl = 0.7691 N Acetamide = 0.3307 N | | | |
|--------------------------------------------|---------------------|----------------------------------------------------------|---------------------|---------------------|--------------------------------------|
| t o min. | Titer 45.95 ccs. | t o min. | Titer 45.53 ccs. | k × 10 ⁶ | k _{Corr.} × 10 ⁶ |
| 1430 | 45.93 | 1444 | 44.24 | 5.25 | 5.14 |
| 4000 | 45.81 | 4121 | 42.50 | 5.11 | 4.83 |
| 8300 | 45.67 | 8281 | 40.14 | 5.18 | 4.83 |
| 10000 | 45.62 | 9783 | 39.22 | 5.39 | 4.99 |
| | | 11400 | 38.47 | 5.40 | 5.06 |
| | | | Mean | 5.27 | 4.97 |

TABLE VII
Acetamide

| Expt. | HCl | %H ₂ O | Amide | NH ₄ Br | NH ₄ Cl | k |
|-------|----------|-------------------|----------|--------------------|--------------------|-------|
| 35 | 0.6355 N | 0.00 | 0.3428 N | — N | 1/2 sat. | 6.39 |
| 41 | 0.7691 | 0.00 | 0.3307 | — | 1/2 sat. | 5.27 |
| 45 | 0.5230 | 0.00 | 0.2508 | — | sat. | 7.22 |
| 57 | 0.5000 | 0.00 | 0.1308 | — | sat. | 7.18 |
| 55 | 0.7432 | 0.00 | 0.3341 | — | — | 5.38 |
| 47 | 0.5577 | 0.025 | 0.1567 | 0.014 | sat. | 8.16 |
| 48 | 0.5555 | 0.025 | 0.1784 | 0.028 | sat. | 7.96 |
| 42 | 0.7055 | 0.04 | 0.2463 | 0.03 | sat. | 8.36 |
| 99 | 0.3287 | 0.06 | 0.1663 | — | 3/4 sat. | 12.35 |
| 102 | 0.4632 | 0.06 | 0.1720 | — | — | 9.86 |
| 68 | 0.3408 | 0.10 | 0.1920 | — | sat. | 11.90 |
| 69 | 0.4629 | 0.10 | 0.1701 | — | — | 9.40 |
| 71 | 0.3877 | 0.10 | 0.2023 | 0.023 | sat. | 10.39 |
| 72 | 0.3764 | 0.10 | 0.1777 | 0.025 | — | 10.40 |
| 73 | 0.3806 | 0.10 | 0.1378 | 0.017 | — | 10.99 |
| 83 | 0.2763 | 0.48 | 0.1414 | — | sat. | 15.63 |
| 85 | 0.3468 | 0.48 | 0.1397 | — | — | 12.30 |
| 89 | 0.3934 | 1.22 | 0.1633 | — | sat. | 14.65 |
| 90 | 0.3302 | 1.22 | 0.1510 | — | — | 17.32 |
| 113 | 0.3659 | 1.30 | 0.1680 | — | sat. | 16.15 |
| 96 | 0.4902 | 2.75 | 0.1674 | — | — | 17.92 |
| 115 | 0.3858 | 2.80 | 0.1539 | — | sat. | 21.05 |
| 116 | 0.3732 | 2.80 | 0.1742 | — | — | 21.13 |
| 103 | 0.4265 | 4.28 | 0.1788 | — | — | 22.27 |
| 104 | 0.3895 | 4.28 | 0.1554 | — | sat. | 22.87 |
| 107 | 0.4759 | 7.58 | 0.1165 | — | sat. | 23.37 |
| 108 | 0.4663 | 7.58 | 0.1165 | — | — | 23.88 |
| 118 | 0.3284 | 12.13 | 0.1582 | — | sat. | 24.64 |
| 119 | 0.4499 | 12.13 | 0.1752 | — | — | 23.79 |

Since the above is a typical example of the acetamide reaction at 25°C the final results only need be given of the other runs. It will be noticed however, and the same was found to hold true for propionamide esterification, that the constants show a definite increasing trend with time. This was the more marked in solutions containing traces of water. The results summarised give however the mean value of the constants, the trend being marked only in a few instances. Table VII presents the data for acetamide and Table VIII those for propionamide. Since in these reactions ammonium chloride is formed only slowly, the condition of the initial solutions with respect to ammonium chloride is noted in the tables as saturated, or otherwise.

TABLE VIII
Propionamide

| Expt. | HCl | %H ₂ O | Amide | NH ₄ Br | NH ₄ Cl | k |
|-------|----------|-------------------|----------|--------------------|--------------------|-------|
| 63 | 0.3529 N | 0.00 | 0.1573 N | — N | sat. | 15.15 |
| 64 | 0.5319 | 0.00 | 0.1352 | 0.029 | sat. | 10.72 |
| 77 | 0.4069 | 0.00 | 0.1516 | — | — | 13.86 |
| 78 | 0.4201 | 0.00 | 0.1303 | — | sat. | 13.85 |
| 80 | 0.3735 | 0.00 | 0.1306 | 0.024 | — | 16.09 |
| 82 | 0.3424 | 0.00 | 0.0990 | 0.026 | sat. | 16.07 |
| 100 | 0.3946 | 0.06 | 0.1494 | — | 3/4 sat. | 14.59 |
| 75 | 0.5268 | 0.10 | 0.1497 | — | sat. | 10.63 |
| 76 | 0.5433 | 0.10 | 0.1391 | — | — | 10.53 |
| 86 | 0.2946 | 0.48 | 0.1217 | — | — | 20.01 |
| 92 | 0.5482 | 1.22 | 0.1259 | — | — | 13.95 |
| 93 | 0.5210 | 1.22 | 0.1415 | — | sat. | 14.50 |
| 112 | 0.4772 | 1.30 | 0.1430 | — | — | 16.44 |
| 97 | 0.5198 | 2.75 | 0.1383 | — | — | 21.63 |
| 114 | 0.4597 | 2.80 | 0.1427 | — | sat. | 22.96 |
| 105 | 0.3486 | 4.28 | 0.1417 | — | — | 29.36 |
| 109 | 0.4883 | 7.58 | 0.0994 | — | — | 27.14 |
| 120 | 0.4703 | 12.13 | 0.1250 | — | — | 27.04 |

In any given experiment with either acetamide or propionamide the deviations from the mean value quoted were usually from 2 to 3 per cent. The degree of reproducibility in different experiments using different preparations is not so good, deviations reaching from 10 to 15 per cent. One disturbing factor which was not fully appreciated at the time of the experiments seems to be that the velocity constant depends on the acid concentration. The constants appear to increase as the acid concentration decreases. Comparison of the experiments in dry alcohol for both amides show this quite definitely. This is in contrast to the more usual case for acid-catalysed reactions where the constants increase though more rapidly than the equivalent concentration of the acid in solution. The constants for propionamide in solutions containing 0.10 per cent water are on this account probably much too low since the HCl concentration is here considerably higher than in other experiments.

Despite the limitations of the data, a very significant and important conclusion can be drawn. The addition of water accelerates the esterification of amides in alcohol. This is probably the first case of this kind for a polar solvent where the catalysing acid is largely ionised.

It may be objected that formamide does not give such a pronounced acceleration as the others, in fact its activity seems to be decreased quite rapidly in the region between 0.5 and 1.2 per cent of water. This however as has already been pointed out is only apparent due to the succeeding hydrolysis of the ethyl formate giving free formic acid which colors the methyl orange, but which is weak enough that it cannot be satisfactorily titrated with this indicator (Its dissociation constant is 2.14×10^{-4}). Other available indicators which would change in a lower (more acidic) pH range than that of a formic acid solution, failed to give an end point that was entirely satisfactory. It is to be concluded therefore that a measurement of the esterification of formamide alone would give increasing rates with increasing water concentrations much beyond the range actually observed.

In the case of acetamide and, considering the acid effect, in that of propionamide also, the rate of esterification reaches a maximum value for from 8 to 12 per cent by weight of water. Over this range the values remain approximately constant. It does not appear as though any special significance can be attached to the position of the maximum.

The concentrations of added neutral salt are small in all cases, the ammonium bromide being about 0.03 N and the chloride reaching 0.11 N. If the solutions had been more dilute and aqueous the formula of Brønsted might have been used. Lack of knowledge however of activity values in the alcoholic solutions used precludes this. Nevertheless arguing that the reactions studied belong to Brønsted's Type O, a linear salt effect of approximately 2 per cent in decinormal solutions might be expected. Such an effect

TABLE IX

| HCl = 0.3287 N t | Amide = 0.1663 N Titer | H ₂ O = 0.06% k × 10 ⁶ |
|---------------------|--------------------------------|-------------------------------------------------|
| 0 min. | 17.65 ccs. | — |
| 1390 | 17.24 | 11.31 |
| 2675 | 16.83 | 11.23 |
| 5590 | 15.99 | 11.70 |
| 7210 | 15.59 | 11.80 |
| | NH ₄ Cl appeared | |
| 8555 | 15.14 | 12.71 |
| 9990 | 14.86 | 12.49 |
| | Solid NH ₄ Cl added | |
| 11400 | 14.54 | 12.65 |
| 12850 | 14.17 | 13.15 |
| 17330 | 13.40 | 13.17 |
| 18330 | 13.22 | 13.31 |
| 19900 | 12.99 | 13.29 |

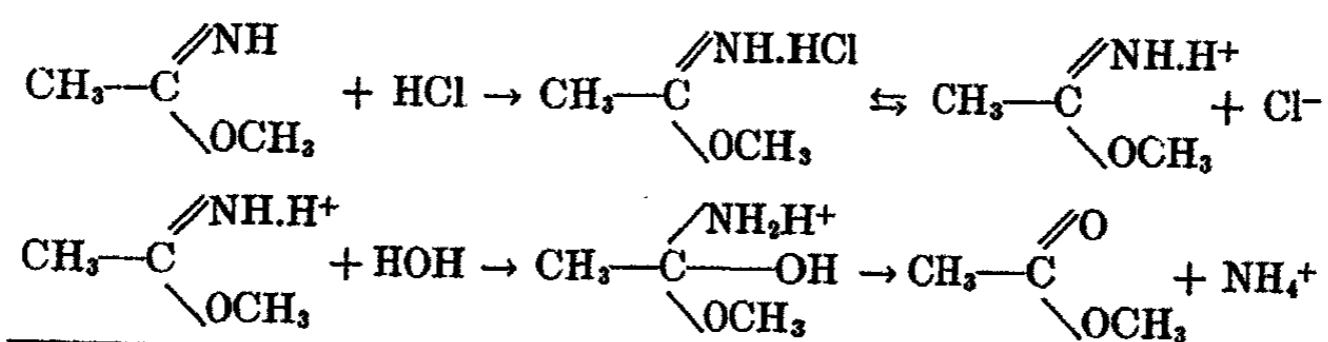
would hardly appear definitely in the results quoted since it would be within the limits of experimental error. Since ammonium chloride however is continually formed one would expect a slightly increasing trend in the constants calculated. This does actually occur, but the fact that it continues after ammonium chloride has precipitated shows the effect to be due to some other cause than the increase of neutral salt present. One other possibility exists of an effect of the presence of excess ammonium chloride, namely that the solid might lead to a heterogeneous esterification on the surface. That this does not occur appreciably is shown by the data in Table IX using acetamide as reactant.

The solution used was approximately three-quarters saturated with ammonium chloride initially. No really marked change is observed as the salt first makes its appearance, nor is there such when a large excess of solid was added. The above conclusions are therefore justified. Moreover the fact that the increasing trend in the constants was not observed in the experiments in absolute alcohol in absence of ammonium chloride initially, precludes the possibility of its being due to the salt.

Discussion of Results

The most important question set forth by these results appears at once to be why water accelerates some reactions and retards others. Reaction kinetics in general are expected to furnish information on the mechanism of the process studied but where several different mechanisms are possible all leading to the same order of velocity constant, the expectation is an ideal to be approached rather than attained with certainty.

From the remarks at the commencement of the paper it may be judged with reasonable certainty that the answer to the above question lies in the nature of the substrate and its possible addition complexes. Whatever be the nature of the catalyst, it is not likely that any explanation would be forthcoming from that alone, since the catalyst will always be the same in a given environment, where it has been seen water in some cases retards and in others accelerates the reaction proceeding. Before offering a possible explanation it would be well to consider some suggestions of Stieglitz¹ with reference to the mechanism of hydrolysis of imido esters. This work seemed to show that a positive ion of the substrate was the reactant. Acids add to the esters to form salts, for they are weak bases and the resulting salt ionises. The ester ion, or ester-H⁺ ion complex subsequently hydrolyses to give the NH₄⁺ ion and the oxygen ester, which may be represented



¹ J. Am. Chem. Soc., 32, 221 (1910); 35, 1774 (1913); Am. Chem. J., 39, 29, 402 (1908).

A similar series of changes are also possible for the hydrolysis of oxygen esters. Stieglitz therefore suggests that the catalytic effect of the acid is due to the transformation of a weak base, the ester, into a stronger base, ammonia.

It seems possible to extend this idea to the effect of water on various reactions. We may presume that a collision between alcohol and amide molecules giving rise to an addition compound precedes esterification. If such complexes are rendered more unstable by the presence of water, the reaction in this case would be accelerated. To accomplish this the water may unite with the reaction products to form more stable compounds. For example the addition of water to the nitrogen atom of the amide group in the amide-

alcohol complex would yield $\left[\begin{array}{c} \text{H} \\ | \\ -\text{NH}_2 \\ | \\ \text{OH} \end{array} \right]$, which on separating would give rise

to ammonia hydrate or on collision with a hydrogen ion, an ammonium ion and water. The passage then from the weak base, the amide, to the more basic ammonia would be accompanied by an acceleration in presence of water. In acid esterifications where the reaction is from the strong base, the alcohol, to the weaker base, the ester, the water molecule would have the reverse effect from the above and attach itself to the acid part of the complex leading to the separation of the more stable alcohol rather than the ester. The same would be true in the diazo-ester decomposition, or in the halogenation of acetone, water in the latter case preventing a hydrogen ion from wandering from the methyl to the carbonyl group by satisfying the secondary valences of the latter.

Consequently when water makes the critical reaction complex more unstable towards reactants than resultants, that is, more apt to break up into resultants than reactants then an acceleration is to be expected. If the reverse is true a retardation may be looked for. The results of Taylor and Close previously mentioned would form such a case since here addition of water to the hydroxy acid, probably to the carboxyl grouping, would render the hydroxyl group still more labile for the formation of the inner ester, the lactone. The results of Kailan and Neumann for the same process in alcoholic solutions cannot be explained on this basis. The fact however that under such conditions both esterification and lactone formation may occur complicates matters further and the correction applied for the esterification, which must of necessity be an approximation, may not be completely satisfactory leaving the net effect of water as that in acid esterification, namely the retardation which they actually observed.

Summary

1. The velocity of esterification of three aliphatic amides in dry and aqueous alcoholic solutions, has been investigated, using hydrogen chloride as a catalyst.

2. The reactions show the kinetics of a bimolecular process. Formamide possibly contains a tautomer which catalyses its esterification.
3. Small concentrations of neutral salt do not show any marked effect on the reaction velocity.
4. Addition of small amounts of water accelerates the reactions, a maximum effect being reached between 8 and 12 per cent. A possible explanation of the inhibiting or accelerating action of water on different reactions has been offered.

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EFFECT OF NON-ELECTROLYTES ON THE STABILITY OF COLLOIDS. I

Arsenious Sulphide Sol

BY SUBODH GOBINDA CHAUDHURY

Introduction

Recently a number of papers have been published, dealing with the effect of non-electrolytes on the stability of colloids. The earlier view that colloids are sensitised in presence of a non-electrolyte due to the diminution of the dielectric constant cannot be upheld in view of these recent researches¹. It was pointed out in the last-mentioned paper¹, that the stability of a sol in presence of a non-electrolyte is not determined by the valency of the precipitating ion as assumed by Kruyt and van Duin and that the change in adsorption of barium ions, observed by Weiser (*loc. cit.*) does not permit us to draw any conclusion as to the decrease in stability because the adsorbed barium ion may be present either in the mobile or in the fixed sheet of the double layer.

These criticisms have been more than confirmed by Sen² with MnO_2 sol. He has shown that the conclusion of Weiser that the adsorption of non-electrolytes by the particles of a sol cuts down the adsorption of precipitating ions is not general. Thus though sugar stabilises a MnO_2 sol toward coagulation, the adsorption of copper ions instead of decreasing increases in presence of sugar. Mukherjee and Chaudhury³ have shown that the rate of migration of the particles does not at all indicate the coagulating concentration of a large number of acids. They pointed out that the effect of the diminution of the dielectric constant is two-fold. It brings about (1) a greater repulsive force between the colloidal particles—which will stabilise the sol and (2) an increased electrical adsorption of oppositely charged ions by the colloid, which will sensitise the sol.

The net effect will depend on the magnitude of these two factors.

The subject, however, requires further study. In the present paper it is intended to discuss the other possible factors that might affect the stability of a sol in presence of a non-electrolyte. It is apparent that for a clear understanding of the effect of a non-electrolyte on the stabilisation of a colloid towards coagulating electrolytes, we must have a more definite knowledge of the factors that influence the flocculation values of electrolytes. The fundamental idea that coagulation takes place at or below a critical potential⁴ is itself open to objection. In fact Powis records that the critical potential

¹ Kruyt and van Duin: *Kolloidchem. Beihefte*, 5, 287 (1914); Weiser: *J. Phys. Chem.*, 28, 1253 (1924); Mukherjee, Chaudhury and Mukherjee: *J. Indian Chem. Soc.*, 3, 349 (1926).

² *Kolloid-Z.*, 38, 310 (1926).

³ *J. Indian Chem. Soc.*, 2, 307 (1925).

⁴ Powis: *J. Chem. Soc.*, 109, 734 (1916).

depends on the nature of the electrolyte added. His method (Burton's U-tube method) is open to serious objections¹. Even allowing for the error inherent in the method, it would seem from the considerations set forth that salts of uni-univalent ions should coagulate a sol at a higher potential than other salts. It is of course clear that coagulation takes place at a lower density of electrical charge in presence of an electrolyte than that of the original colloid, and that below a certain potential (possibly different for different electrolytes for the same sol) cohesive forces are active in causing the particles to agglomerate. Moreover similarly charged ions have more or less stabilising effects, though generally not as marked as effects of oppositely charged ions. The net effect of these factors will determine the coagulating power of an electrolyte for a definite concentration of the colloid.

Effect of Non-electrolytes

Let us now examine more closely how a non-electrolyte may affect the various factors, which determine the stability of a colloid towards electrolytes. The non-electrolyte may change:

(1) The dielectric constant of the medium and (a) hence the electrical forces between the particles when they approach one another closely and (b) also the electrical adsorption of oppositely charged ions as defined by Mukherjee².

(2) The specific adsorbabilities of the ions on the surface of the colloidal particles.

(3) The cohesive forces operative in the system.

Before discussing the effect of the change of each one of these factors, it must be emphasized that the nature of the non-electrolyte determines which of the above mentioned factors will predominate for a particular sol and a particular electrolyte. Neglecting for the present chemical changes that might result from the addition of a non-electrolyte we shall only consider simple physical changes that occur in its presence and see how far these simple considerations suffice to explain the results obtained.

1. *Effect of the change of the dielectric constant.* A diminution in the dielectric constant of the medium diminishes the osmotic coefficient or the degree of the dissociation of the electrolyte employed. The electrical adsorption of the oppositely charged ions will also be increased (Mukherjee and Chaudhury: loc. cit.) provided *no specific action takes place between the colloidal surface and the ions present.*

If the surface has specific attraction for similarly charged ions, this specific adsorption will be retarded on account of the decrease in the osmotic coefficient. Also electrical repulsion between the similarly charged ion and the surface will increase, thereby diminishing the number of collisions for the same concentration and temperature. This effect will tend to sensitise the sol, provided of course the specific attraction does not change with the dielectric

¹ Mukherjee: Proc. Roy. Soc., 103A, 102 (1923).

² Faraday Soc. Discussion, October (1920).

constant. So for a simple case, where there is no specific attraction, a diminution in dielectric constant will lower the osmotic coefficient but increase the adsorbability and thus bring into play two opposing factors.

In general, however, when similarly charged ions are weakly adsorbed we might neglect the change in adsorbability of these ions on the addition of non-electrolytes. Finally a diminution in dielectric constant in the medium will bring greater repulsive forces into play between the colloidal particles and consequently the actual coalescence of the particles will be retarded. This will tend to stabilise the sol. Thus the resultant effect of these three factors will determine, whether a colloid will be stable or unstable on changing the dielectric constant.

(2) *Change of the specific adsorbability on the addition of a non-electrolyte.* If the specific adsorbability as apart from the electrical adsorption of the precipitating ions changes, then the stability will depend on the resultant effect of these changes. As a result there might be widely different changes in the flocculation values of different electrolytes on the addition of the same non-electrolyte. In the case of electrolytes with complex cations and anions this possibility has to be remembered.

(3) Another important change is brought about by the addition of a non-electrolyte, namely in the value of the interfacial tension between the colloidal particles and the surrounding medium. Though the role of solid-liquid interfacial tension in the formation¹ and in the coagulation of colloids² has long been recognised, one scarcely finds any reference to it in recent literature on the coagulation of suspensoids, perhaps partly because it is not possible to determine the tension of solid-liquid interfaces, and partly because the actual part played by this factor in the coagulation of colloids is not clear except that the greater the interfacial tension, the greater will be the tendency for the coalescence of particles and that a lowering of the interfacial tension will thus tend to make the dispersed state relatively more stable. But no very great stress has been laid on the rôle of surface tension in the process of coagulation. Now if we assume a parallelism between the liquid-vapour surface tension and solid-liquid interfacial tension³ we can explain many anomalous results in this subject. We see that in a medium, where this interfacial tension is greater, the stability of the colloid will be relatively less and the sol will be stable so long as the electrical forces preventing coalescence remain sufficiently effective. That is, the sol will be sensitive to electrolytes as it will coagulate even when the electric charges remain comparatively higher. When the interfacial tension is lower, the colloidal particles will coagulate at a lower potential. We may say that in the former case the sol is sensitised and in the latter case the sol will be stabilised. No one has yet given any explanation as to why critical potentials with As_2S_3 sol and monovalent precipitating ions are generally higher than those found with di-, tri- and tetravalent precipitating ions (Powis: loc. cit.). The critical potential

¹ Donnan: *Phil. Mag.*, (b) 1, 647 (1901).

² Duclaux: *J. Chim. phys.*, 7, 405 (1909).

³ Cf. Freundlich: "Colloid and Capillary Chemistry", 192.

ought to be a little higher in the case of uni-univalent electrolytes because of the higher interfacial tension produced by the corresponding salts of uni-valent cations at the high concentrations required to coagulate the sol.

This view seems to be in agreement with some observations of ours. From the above considerations we can also see why in presence of non-electrolytes with lower surface tension, adsorbability and coagulating powers cannot go hand in hand. If we assume that coagulation takes place at a lower critical potential on account of the smaller surface tension and as the dielectric constant also diminishes, (as is frequently the case on the addition of non-electrolytes) then we can understand that even when the adsorbability of the precipitating ion increases the sol may appear to be stabilised against coagulation as more of the coagulating ion must be adsorbed to bring down the potential to the lower critical value. We thus see that if the coagulating potential becomes sufficiently low, then in spite of the greater adsorbability of the precipitating ion, a higher concentration will be necessary for coagulation, that is, a lower coagulating power will be observed. These considerations explain the apparent paradox of increased adsorbability and lower coagulating power, referred to by Dhar and co-workers¹. Sen (loc. cit.) has observed that sugar stabilises a manganese dioxide sol whereas he finds from adsorption experiments with precipitated MnO_2 that the adsorbability of the precipitating ion increases in presence of sugar. This consideration brings out strongly the futility of the comparison between adsorption as measured with precipitated colloids and the coagulating power of electrolytes.

To sum up, we can say that the addition of a non-electrolyte brings two physical factors into play.

1. A diminution in dielectric constant, the effect of which is generally to sensitise the sol.
2. An alteration in the interfacial tension which influences the electrical potential below which coagulation takes place.

In this paper, an attempt has been made to correlate some observations with As_2S_3 sol.

The present work was undertaken to experimentally test the views developed above. It is claimed that convincing data have been given to show the general individuality of the fundamental assumptions of a constant critical potential in presence of coagulating electrolytes. Also the diversity of observations with the same sol and the same non-electrolyte with different electrolytes can only be explained by assuming a change in critical potential (compare also earlier publications from this laboratory).

Experimental

As₂S₃ Sol and Methyl and Ethyl Alcohols.

(a) *Adsorbability as measured analytically and coagulating power:*

From what has been written in the introduction one should not in general expect a direct parallelism between adsorbability and coagulating power, specially in presence of non-electrolytes.

¹ J. Phys. Chem., 26, 701 (1922); 28, 313 (1924); 29, 435, 659 (1925); Kolloid-Z., 34, 262 (1924); 36, 129 (1925).

The following coagulations and adsorption experiments were done with arsenious sulphide sol in presence of methyl and ethyl alcohols with BaCl_2 as the coagulating electrolyte. In the adsorption experiments, 50 c.c. of 0.0025N BaCl_2 were added to a mixture containing 25 c.c. of the sol and 25 c.c. of water or instead of water 25 c.c. of aqueous alcohol solution. The mixtures were kept for 24 hours and then the amount of barium in a portion of the clear supernatant liquid was estimated as sulphate. From this the amount in 100 c.c. was calculated. Tables I-II contain the experimental results:

TABLE I
Arsenious sulphide sol and methyl alcohol

| Percentage by volume of MeOH | Coagulating concentration in normality | Amount of adsorption of barium in gms. by 25 c.c. of the sol |
|------------------------------|----------------------------------------|--------------------------------------------------------------|
| 0% | 0.001834 | 0.001352 |
| 10% | 0.001624 | 0.001135 |
| 25% | 0.001286 | 0.001154 |

TABLE II
Arsenious sulphide sol and ethyl alcohol

| Percentage by volume of EtOH | Coagulating concentration in normality | Amount of adsorption of barium in gms. by 25 c.c. of the sol |
|------------------------------|----------------------------------------|--------------------------------------------------------------|
| 0% | 0.001911 | 0.001352 |
| 10% | 0.002278 | very small |
| 25% | 0.002940 | 0.00063 |

It will be seen from these tables that the sol is sensitised against barium chloride although the adsorption at first increases, and then decreases. Similarly in the case of ethyl alcohol, though the sol is stabilised against barium chloride all along, the adsorbability of barium decreases more in 10% EtOH than in 25% EtOH. So a parallelism between adsorbability and coagulating concentration does not always hold good in presence of these alcohols as is to be expected from the theoretical considerations set forth in the introduction.

(b) *Relation between adsorbability as deduced from charge measurements and coagulating power and the effect of the dielectric constant on the adsorbability of the precipitating ions:*

Tables III and IV contain the values of migration velocities of arsenious sulphide sol with different concentrations of hydrochloric acid in presence of methyl and ethyl alcohols. (cf. also Mukherjee, Ray Chaudhury and Chaudhury to be published shortly and Mukherjee and Chaudhury: Proceedings Indian Science Congress, January, 1927). Table V contains the coagulating concentrations of hydrochloric acid in presence of methyl and ethyl alcohols. The rate of migration (V) has been expressed in cms. per sec. per volt/cm.

TABLE III
Arsenious sulphide sol and ethyl alcohol
Temperature 35°C.

| % EtOH by volume | Conc. HCl, 0.0158 N $V \times 10^6$ | Conc. HCl, 0.0079 N $V \times 10^6$ |
|---------------------|----------------------------------------|----------------------------------------|
| 0.0 | 43.5 | 47.3 |
| 2.5 | 38.7 | 46.3 |
| 5.0 | 35.0 | 44.4 |
| 10.0 | | 40.2 |

TABLE IV
Arsenious sulphide sol and methyl alcohol

| % MeOH by volume | Conc. HCl, 0.00N $V \times 10^6$ | Conc. HCl, 0.005 N $V \times 10^6$ | Conc. HCl, 0.01 N $V \times 10^6$ |
|---------------------|-------------------------------------|---------------------------------------|--------------------------------------|
| 0.0 | 56.5 | 47.0 | 43.5 |
| 2.5 | 56.8 | 41.8 | 40.5 |
| 5.0 | — | 39.0 | 38.3 |
| 10.0 | — | 36.0 | — |

It will be seen from the tables, that, for the same concentration of hydrochloric acid as higher percentages of ethyl and methyl alcohols are employed, the velocity diminishes. Consequently since change in osmotic coefficient can only diminish the amount of adsorption, the lower charge, observed as higher percentages of alcohol are employed, leads us to assume a marked increase in the adsorbability of hydrogen ions, and that the increased adsorption more than counteracts the effects of the non-electrolyte in diminishing the osmotic coefficients. These results strongly support the theory of electrical adsorption of Mukherjee wherein the energy of adsorption is given as $W = N_1 N_2 E^2 / XD$ where N_1 and N_2 are respectively the valencies of the primary and the electrically adsorbed ions; E is the electronic charge; X is the distance between the centres of the ions at closest approach on electrical adsorption and D , the dielectric constant of the medium between the ions. There is thus also a definite evidence of the existence of a solvent layer between the ions (Vide Proceedings Indian Science Congress, loc. cit.).

TABLE V
Arsenious sulphide sol

| Percentage conc. of alcohol | Coagulating concentration of HCl in presence of | |
|--------------------------------|-------------------------------------------------|---------------|
| | Methyl alcohol | Ethyl alcohol |
| 0.0 | 0.04450 | 0.03800 |
| 2.5 | 0.04325 | 0.03675 |
| 5.0 | 0.04225 | 0.03525 |
| 10.0 | 0.04050 | 0.03400 |
| 25.0 | 0.03550 | 0.03500 |

From the above tables we see a parallelism between the diminution of charge and coagulating concentrations. At 25% ethyl alcohol, the coagulating concentration of HCl increases a little although it is less than the coagulating concentration of HCl alone and than that in presence of 2.5% ethyl alcohol. The dielectric constants of methyl and ethyl alcohols are 31.5 and 20.8 (18°C) respectively and their surface tensions are 23.02 and 22.03 (20°C). That at higher percentages the sol in presence of ethyl alcohol tends to be stabilised shows that the effect of surface tension is being felt there.

Potential near the coagulating concentrations.

The following table contains the migration velocity in volts per cm. per unit potential gradient near the coagulating concentration of the electrolytes (obtained by cataphoretic experiments).

TABLE VI

| Electrolyte | Rate of migration |
|-------------------------|-------------------|
| HCl N/40 | 38×10^6 |
| KCl N/30 | 36×10^6 |
| BaCl ₂ N/800 | 27×10^6 |

From the slope of the curve between the rate of migration and the concentration it would appear that the differences in the rates will persist up to the coagulating concentration in agreement with the considerations set forth in the introduction.

Conclusion

(1) Measurements of the coagulation potential of As₂S₃ sol with potassium chloride, barium chloride, and hydrochloric acid have been done. The potential with uni-univalent electrolytes is higher than that with barium chloride. An explanation is advanced that the interfacial tension at the colloid-liquid-interface being greater in the case of these salts at their precipitation concentrations, they should show higher coagulation potentials.

(2) It has been shown that adsorbability as measured analytically and coagulating power do not go hand in hand. Explanations based on the change of dielectric constant and interfacial tension have been advanced.

(3) The effect of dielectric constant has been shown, by measurements of the rate of migration of arsenious sulphide sol in presence of hydrochloric acid with methyl and ethyl alcohols, to be, in general, to sensitise the sol.

My best thanks are due to Prof. J. N. Mukherjee for his advice and facilities for work.

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19-103

NEW HIGH-TEMPERATURE FIXATION REACTIONS OF NITROGEN

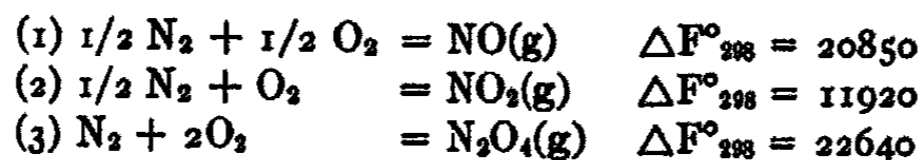
BY NORMAN W. KRASE AND BILL MACKEY*

The remarkable growth of industries based on the fixation of atmospheric nitrogen during the past fifteen years has few parallels in history. In 1910 a total of 9000 tons of atmospheric nitrogen was fixed; the production rising to 600,000 tons in 1925. Of the 1925 production, 6.7 percent were fixed by the arc process, 30.3 percent by the cyanamide process and 63 percent by the direct synthetic ammonia process. Present developments clearly show that the last named will further increase in popularity.

A careful consideration of the synthetic ammonia process will incite in one a feeling of doubt that the last word has been said or that future developments will be only improvements in the details of existing processes. Research and development have carried the operations into the field of high temperatures and extremely high pressures. Enormous technical difficulties have been overcome and continued success seems certain. When it is realized that the micro-organisms in the soil fix atmospheric nitrogen at normal temperature and pressure on a scale far beyond what we may hope to attain commercially in the near future, it seems well to give thought to other methods of attacking the general problem. In particular is it desirable to exhaust the obvious possibilities of existing data as a guide to future research.

Practically the only avenue by which we can approach the general problem of nitrogen fixation is that of thermodynamics. The principles and methods of this subject have received wide exploitation in several branches of chemistry and its potential use in enabling predictions to be made with regard to chemical reactions has been ably demonstrated.¹ The well known procedure of deriving new equilibrium data by the combination of several known equilibria is the method employed. An attempt has been made to indicate to what extent a given conclusion is unreliable by pointing out, for example, the range of extrapolation of data and the assumptions involved in a given calculation.

A consideration of nitrogen-fixing reactions may well begin with those in which oxygen is concerned. The many important compounds such as nitric acid and its salts are of major importance in modern industry. A glance at the data showing the free energy of formation of the nitrogen oxides reveals the fact that all are unstable and tend to decompose and liberate nitrogen. The data at ordinary temperature and pressure are as follows:—



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¹ Lewis and Randall: "Thermodynamics and the Free Energy of Chemical Compounds".

Investigation of these reactions over a wide range of temperature showed that NO becomes more stable with respect to its elements at very high temperatures. The arc process of nitrogen fixation demonstrates the feasibility of establishing equilibrium at a high temperature and by sudden cooling produces a gas at ordinary temperature containing vastly more than its equilibrium concentration of NO. The slow rate of decomposition of NO at room temperature makes it for all ordinary purposes a stable compound. The arc process using air as a source of nitrogen and oxygen yields a gas containing from two to three percent NO by volume. This dilute gas is scrubbed with water or alkali and the process yields dilute nitric acid or a nitrate. Much of the cost of producing fixed nitrogen by the arc process results from the necessary use of dilute nitrose gas for absorption in water or alkali. Proposals to increase the concentration of NO in arc gas by the use of enriched air or by the use of N_2 and O_2 in the stoichiometric proportions have been made. Calculations on reaction (1) can best be made by use of the data obtained by Nernst¹ using air. Table I shows the concentration of nitric oxide in percent by volume at equilibrium as a function of temperature. The results from 1811° to 2675° absolute are experimental values of Nernst using air. The calculations at higher temperatures and those for stoichiometric proportions of nitrogen and oxygen were made using the relation²:

$$(4) \Delta F^\circ = 21600 - 2.50 T$$

and the relation:

$$(5) F^\circ = -RT \ln K$$

Equation (4) is developed³ from the data of Nernst, Thomsen and Berthelot's value of 21600 calories as the heat of reaction, and the assumption that the heat capacities of O_2 , N_2 and NO are the same. The extrapolation is over a range of about 800°.

TABLE I

| Temp. | Percent NO by volume | | Temp. | Percent NO by volume | |
|-------|----------------------|---------------------|-------|----------------------|---------------------|
| | Air | $1/2 N_2 + 1/2 O_2$ | | Air | $1/2 N_2 + 1/2 O_2$ |
| 1811 | .37 | — | 2675 | 2.23 | 2.86 |
| 2033 | .64 | .80 | 3000 | 3.47 | 4.52 |
| 2195 | .95 | — | 3200 | 4.27 | 5.51 |
| 2580 | 2.05 | 2.62 | 3500 | 5.52 | 7.23 |

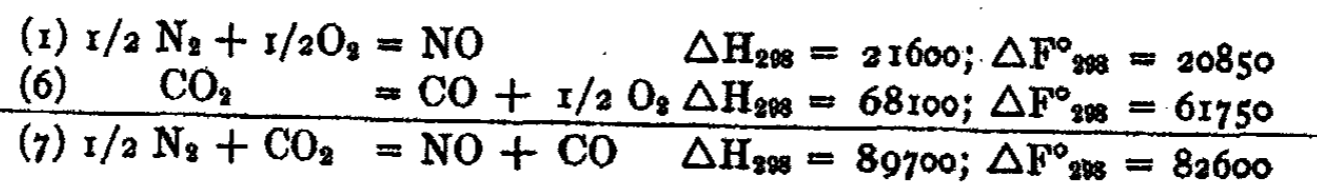
Before considering these results any further we shall discuss some results obtained with another reaction for the formation of NO.

¹ Z. anorg. Chem., 49, 213 (1906).

² "Our attention has been called by one of the authors of recent data on the nitric oxide equilibrium, (Briner, Boner and Rothen: J. Chim. phys., 23, 788 (1926)) to the fact that a new free energy equation has been developed by them on the basis of the new data. This calculation, it appears, involves the determination of the constant in the Nernst equation. In our recalculation, we have followed the more recent terminology of thermodynamics as illustrated in the publications of G. N. Lewis, and have pointed out the effect of the new data on several important related equilibria. This latter was the primary purpose in publishing the recalculated values."

³ Lewis and Randall: loc. cit., p. 560.

This calculation is given in more detail than subsequent ones. If we combine reaction (1) with the reaction expressing the dissociation of CO_2 we get the reaction desired:



$$\Delta C_p(1) = 0$$

$$\Delta C_p(\text{CO} + 1/2 \text{O}_2) = 9.75 + .0015 T$$

$$\Delta C_p(\text{CO}_2) = 7.00 + .0071 T - .00000185 T^2$$

$$\Delta C_p(7) = 2.75 - .0056 T + .00000186 T^2$$

$$\text{Then: } 89,700 = \Delta H_0 + 2.75 \times 298 - \frac{.0056}{2} (298)^2 + \frac{.00000186}{6} (298)^3$$

$$\text{From which } \Delta H_0 = 89137$$

$$\Delta F = \Delta H_0 - 2.75 T \ln T + .0028 T^2 - .00000031 T^3 + IT$$

$$\text{When } T = 298, \Delta F = 82600 \text{ and } I = -7.09$$

$$\text{Then } \Delta F^\circ = 89137 - 6.33 T \log T + .0028 T^2 - .00000031 T^3 - 7.09 T$$

Substituting in values of T which are of interest from the standpoint of the arc process we find the results shown in Table II.

TABLE II

| T | ΔF° | K | % NO |
|------|------------------|-----------------------|-------|
| 2000 | 41920 | 2.64×10^{-5} | .32 |
| 3000 | 18580 | .0444 | 10.88 |
| 3500 | 6602 | .3872 | 23.75 |

The data in Tables I and II and subsequent ones are graphically shown in Fig. 1 where the equilibrium percentage of NO is plotted against the absolute temperature. It is seen that the use of N_2 and O_2 in stoichiometric proportions results in comparatively little improvement over the use of air in the arc process. The use of CO_2 and N_2 in the arc, however, should yield a gas containing at least twice as great a concentration of NO as that obtainable from N_2 and O_2 . This is contrary to the experimental results of Muthmann and Schaidhauf¹ who found that mixtures of N_2 and CO_2 gave the same yield of NO as mixtures of N_2 and O_2 . The conditions of their experiments, however, were not exactly those obtaining in an arc and further tests seem desirable. It should be pointed out that the conclusions of thermodynamic calculations do not indicate that a given result will be obtained—they merely state what result is the true one based on establishment of true equilibrium.

¹Z. Electrochemie, 17, 497 (1911).

Nitrogen, Hydrogen and Carbon

The reactions of nitrogen and carbon with and without the presence of hydrogen are of considerable interest. The formation of cyanogen and hydrocyanic acid are represented by the following equations:

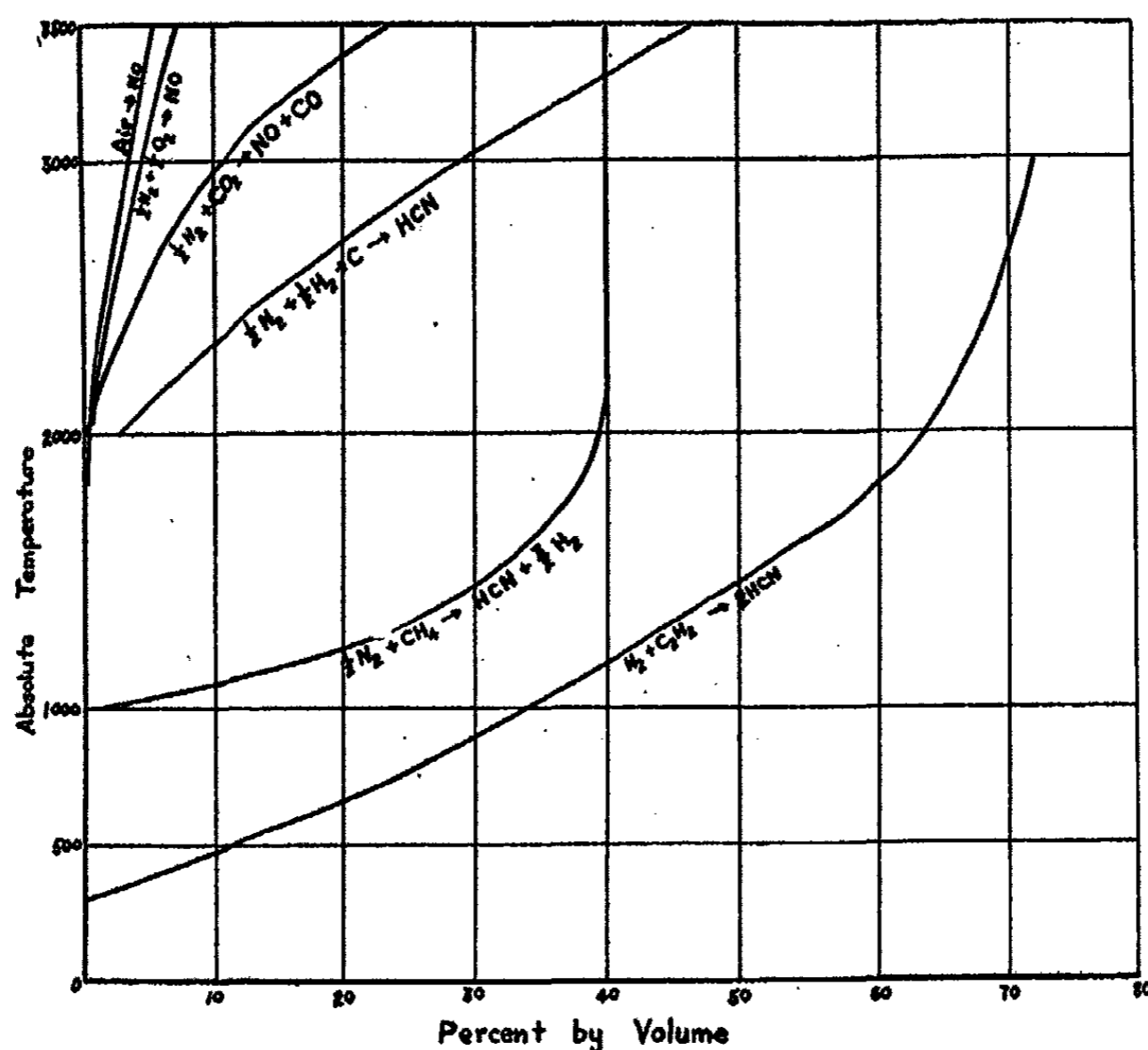
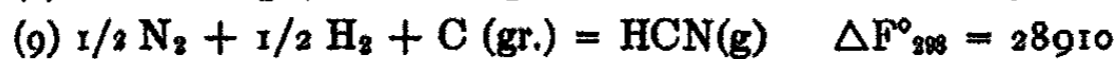


FIG. 1

The data are taken from Lewis and Randall¹. The data for reaction (8) involve some uncertainties for the value of the heat of reaction which is finally estimated as 32,000. The data for reaction (9) are obtained by combination of about twelve equilibrium measurements and compare well with the direct experimental values of von Wartenburg². The use of reaction (8) seems to be without promise at any temperature and accurate calculations of the change of free energy with the temperature cannot be made. Attempts by von Wartenburg to form cyanogen in an arc operating in nitrogen have failed entirely. Apparently cyanogen is completely unstable at all temperatures.

¹ Loc. cit., pp. 590, 592.

² Z. anorg. Chem., 52, 299 (1907).

The measurements of von Wartenburg on nitrogen, hydrogen and carbon permit the formulation of the free energy-temperature equation on the assumption that ΔC_p is zero. This equation is:

$$(10) \quad \Delta F^\circ = 32000 - 10.3 T$$

The experimental data of von Wartenburg are given in Table III.

TABLE III

| T | Percentage HCN |
|------|----------------|
| 1908 | 1.95 |
| 2025 | 3.1 |
| 2148 | 4.7 |

Using equation (10) we have calculated the equilibrium concentrations at temperatures up to 3500°K, an extrapolation of almost 1500°. The calculated results are given in Table IV.

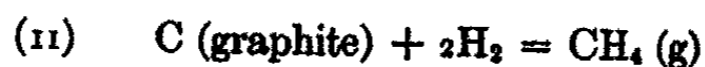
TABLE IV

| T | ΔF° | K | %HCN |
|------|------------------|-----------------------|--------|
| 298 | 28910 | 8.1×10^{-22} | — |
| 1000 | 21700 | 1.9×10^{-6} | .00093 |
| 2000 | 11400 | .0572 | 2.78 |
| 3000 | 1100 | .8321 | 29.4 |
| 3500 | -4050 | 1.785 | 47.2 |

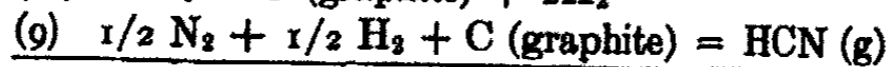
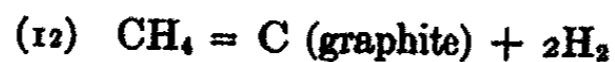
Apparently the use of N_2 and H_2 in an arc struck between carbon electrodes or the use of mixed N_2 and H_2 passed through graphite used as the resistor of an electric furnace should result in the production of gas containing significant quantities of HCN.

Nitrogen and Methane

The use of nitrogen and hydrocarbons at elevated temperatures such as are obtainable in the electric arc furnishes further interesting speculation. In the case of methane reliable equilibrium data exist for its formation from the elements. Pring and Fairlie¹ have measured the equilibrium partial pressures for the reaction:



These results have been considered by Lewis and Randall² and the free energy-temperature relation developed. If we proceed as follows:



¹ J. Chem. Soc., 101, 91 (1912).

² loc. cit., pp. 571-572.

The addition of the free energy equations for reactions (12) and (9) gives the free energy-temperature equation for reaction (13) as follows:

$$(14) \quad \Delta F^\circ = 48,300 - 15.18 T \log T - .0008 T^2 + .0000002 T^3 + 15.7 T$$

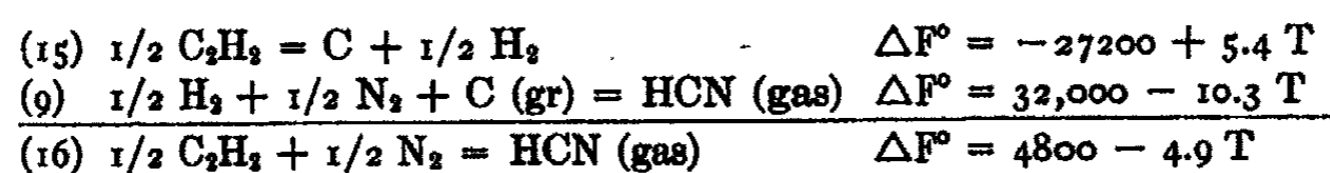
Calculation at a number of temperatures yields the data shown in Table V.

| T | ΔF° | K | %HCN |
|------|------------------|-----------------------|------|
| 298 | 41720 | 1.8×10^{-30} | — |
| 1000 | 17800 | .000132 | 1.0 |
| 2000 | -22118 | 269.2 | 39.4 |
| 3000 | -64748 | 54,830 | 40 |
| 3500 | -85268 | 223,900 | 40 |

It is seen that, if equilibrium is established at 2000° or above, a gas containing 40 percent of HCN and 60 percent of H₂ will result. This temperature permits the reaction to be carried on in other apparatus than the arc furnace and makes possible the employment of catalysts for the establishment of equilibrium. Much work has been reported on different methods of causing nitrogen and hydrocarbons to react and on suitable apparatus for this purpose. There is no question but that the reaction offers extremely interesting possibilities.

Nitrogen and Acetylene

Sufficient data for estimating the results of the high temperature reaction of nitrogen and acetylene¹ exist. Combination of the following relations permits calculation of the yield of HCN:



Substitution of appropriate temperature values yields the data in Table VI.

| Temp. | Kp | %HCN | Temp. | Kp | %HCN |
|-------|--------|------|-------|------|------|
| 298 | .00363 | .018 | 3000 | 5.25 | 72.3 |
| 1000 | 1.05 | 34.4 | 3500 | 5.88 | 74.7 |
| 2000 | 3.52 | 63.8 | | | |

This reaction is of obvious interest and deserves attention from workers in the field of nitrogen fixation.

¹ Francis: Ind. Eng. Chem., 20, 279 (1928).

Summary

Several new high-temperature fixation reactions of nitrogen have been investigated with the aid of thermodynamics. In the case of nitrogen and oxygen only a comparatively small increase in the concentration of nitric oxide results when stoichiometric proportions are used as compared with the result using air. The reaction of nitrogen and carbon dioxide in the arc should produce a concentration of nitric oxide more than double that when air is used.

Three reactions of nitrogen yielding hydrocyanic acid appear to be promising. Nitrogen, hydrogen, and carbon should yield concentrations of HCN exceeding fifteen percent at the usual arc furnace temperature. The interaction of nitrogen and methane to form HCN and hydrogen is complete at 2000° absolute. The combination of nitrogen and acetylene to form HCN is quite marked at relatively low temperatures and should yield a gas containing almost 70 percent HCN by volume at the arc furnace temperature.

THE EFFECT OF SALTS ON WEAK ELECTROLYTES*

II. Calculation of Overlapping Constants¹

BY HENRY S. SIMMS

Introduction

To avoid making the preceding article² too long it seems better to present in a separate paper the potentiometric titration data of polyvalent acids, and to explain the method of calculating the titration indices of those polyvalent acids with overlapping constants.

In a previous paper³ a method was given for calculating titration indices which overlap. This method is accurate only when the ionic strength is the

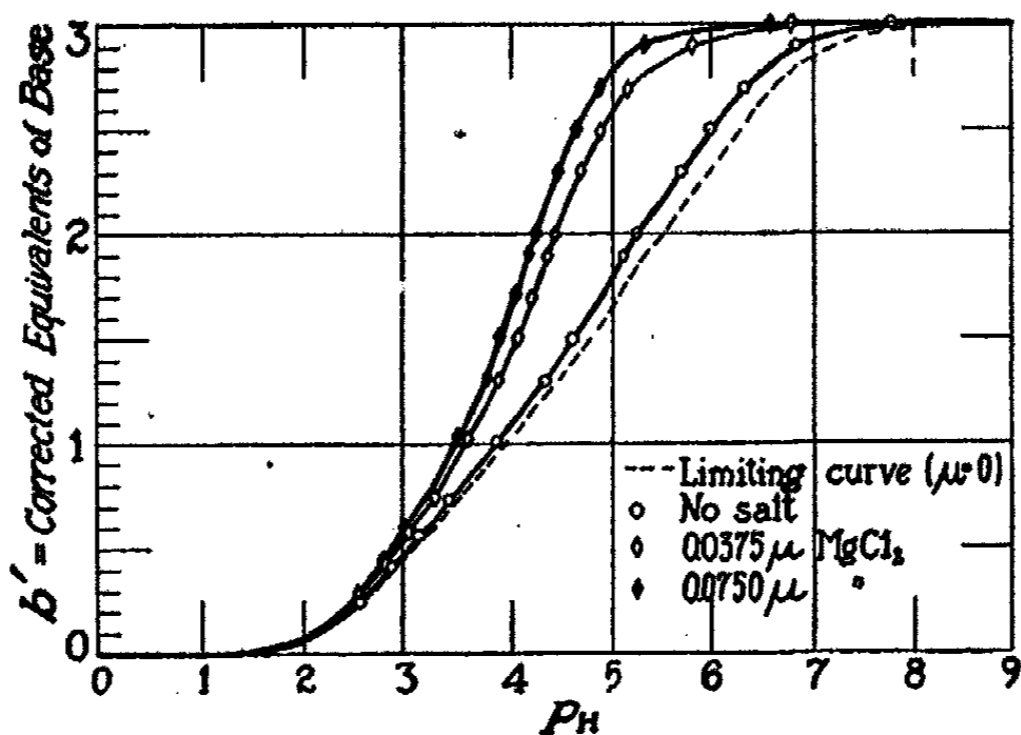


FIG 1

Citric acid titration curve. The dotted curve represents the theoretical curve at zero ionic strength (infinite dilution). Curve 1 is direct titration with NaCl; 2, in the presence of "dilute" MgCl₂; 3, in the presence of "concentrated" MgCl₂. See Fig. 6.

same for all the data. We will review this method, as applied to a divalent acid, below. In the study of activity coefficients it was necessary to devise a method to calculate accurate titration indices from data with various ionic strengths. This will also be presented below together with data on several divalent acids and one trivalent acid. An example of such data is found in

* From the Department of Animal Pathology of The Rockefeller Institute for Medical Research, Princeton, N. J.

¹ The term "overlapping" constants (or indices) in distinction from "isolated" constants is used when the titration indices are less than 2.5 index units apart. Thus $PG_2' - PG_1' = 0.66$ for azelaic acid (at an ionic strength of 0.01μ); hence the constants are "overlapping". On the other hand the difference between the titration indices of oxalic acid is 3.03, and the constants or indices are "isolated".

² Simms: J. Phys. Chem., 32, 1121 (1928).

³ Simms: J. Am. Chem. Soc., 48, 1239 (1926). See corrections in footnote 1 of the preceding article.

Fig. 1 for citric acid, which illustrates the magnitude of the effect of salts. These data can at present be calculated only with the use of the method described in section III.

II. Review of Method of Calculation of Titration Indices of a Divalent Acid from Data with Constant Ionic Strength

First—Plot the experimental H^+ ion indices (P_H) against the corrected equivalents of base⁴ (b'),

$$b' = \frac{b - a + h - oh}{c} \quad (I\ 34)$$

(as in Fig. 1 of the above paper³) and estimate graphically the approximate titration indices⁵ (P_{G_1}' and P_{G_2}').

Second—For each experimental point in the buffer range of the titration index which we wish to calculate (say P_{G_1}') subtract the H^+ ion index (P_H) from the *other* tentative titration index (P_{G_2}') and calculate the corresponding α value (α_1) from the equation:⁶

$$P_H - P_G = \log \frac{\alpha}{1 - \alpha} \quad (1)$$

Third—By subtracting this value of α_1 from b' we get α_2 , since (from I 33):

$$b' = \alpha_1 + \alpha_2 \quad (2)$$

Fourth—The titration index in question (P_{G_1}') may be calculated from α_2 by Equation 1.⁶

This calculation is made for all points in the buffer range of the titration index in question (P_{G_1}') and the average of these index values may be used (in place of the tentative value) to calculate the other index (P_{G_2}) by repeating the process (i.e., calculate α_2 for points in the lower buffer range; subtract them from b' to get α_1 ; and calculate P_{G_1}' from α_1).

⁴ When great accuracy is not required (or when the correction is small) the activities h and oh may be used in place of the concentrations h and oh :

$$b' = \frac{b-a}{c} + \frac{H-OH}{c} \quad (\text{approximately}) \quad (I\ 35)$$

The notation is the same as in the previous articles.

b' = corrected equivalents of base.
 $(b-a)/c$ = equivalents of base.
 b = molar concentration of strong base.
 a = " " " " acid.
 h = " " " " hydrogen ion (H = activity).
 oh = " " " " hydroxyl ion (OH = activity).

⁵ This may be done most easily with a paper mold cut the shape of a typical monovalent dissociation curve (Equation 1). Values of $\log \alpha/(1-\alpha)$ for various values of α may be found in W. M. Clark: "The Determination of Hydrogen Ions", p. 460 (1922). This paper mold should be applied to the upper and lower parts of the titration curve and the two curves drawn (with pencil) in such a way that the sum of α_1 and α_2 of the two curves should equal b' (of the experimental curve) at each P_H . The center ($\alpha=0.5$) of each of these monovalent curves will thus give a tentative titration index which may be used in the succeeding steps.

⁶ This may be obtained easily from a large scale plot of α against $\log \alpha/(1-\alpha)$ (see footnote 5).

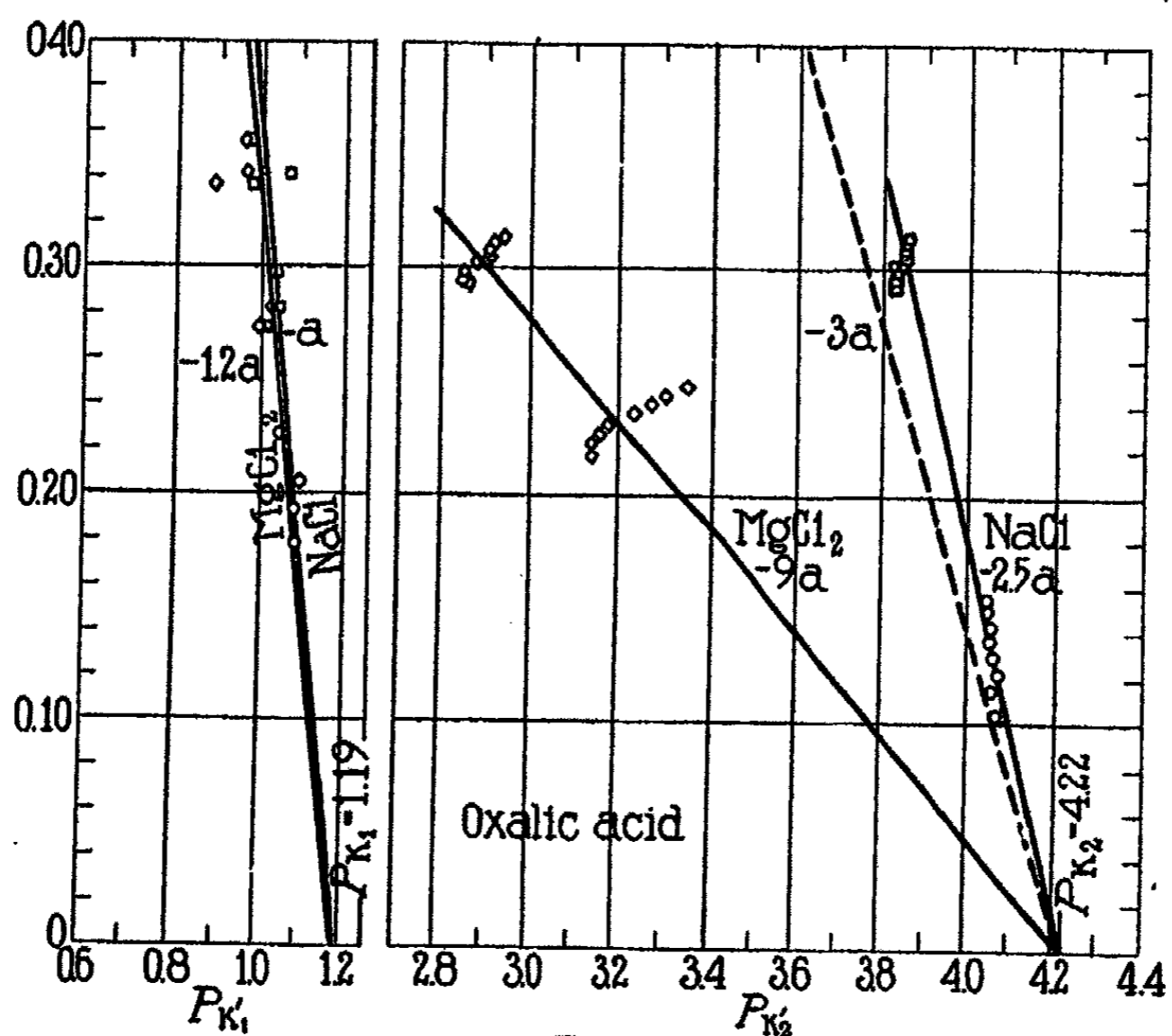


FIG. 2
Oxalic Acid

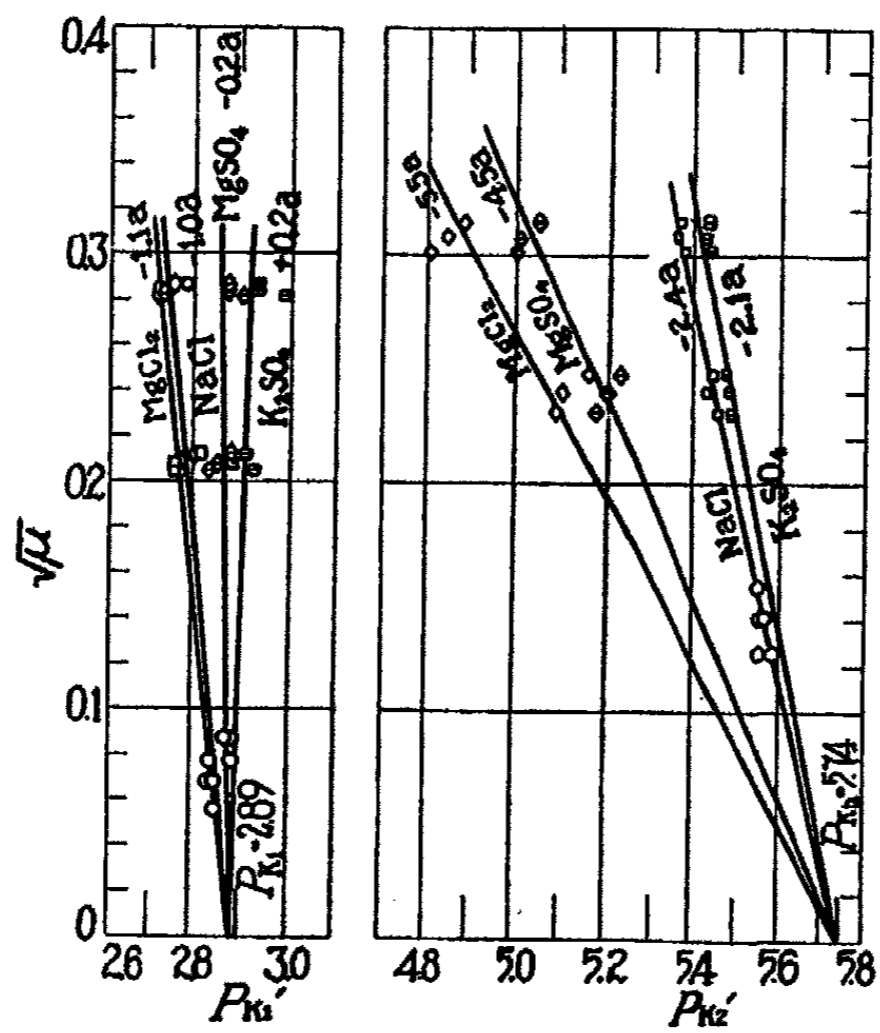


FIG. 3
Malonic Acid

For bases, ampholytes and substances with more than two overlapping indices see the above paper,³ p. 1245.

If the calculated indices differ materially from the tentative ones, the process should be repeated using the calculated indices to obtain more accurate values.

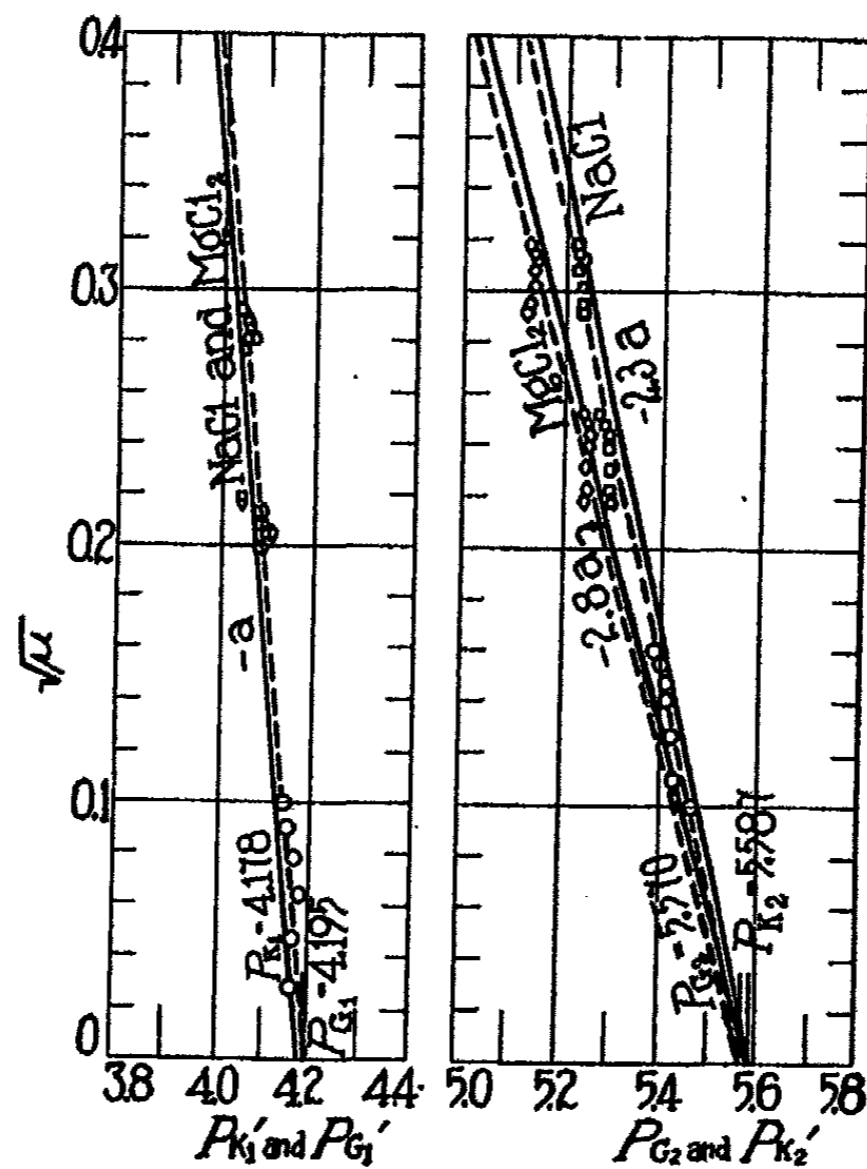


FIG. 4
Succinic Acid

If, as is likely to be the case, the ionic strength is not constant, the titration indices found above will not be correct and the method described below may be used to obtain more accurate values.

III. Method of Calculation of Titration Indices from Data at Different Ionic Strengths

For this procedure it is advisable to have data over a wide range of ionic strengths (below 0.1μ) in the presence of univalent ions, unless the substance is sufficiently similar to those which we have studied to permit estimating the slopes of the curves.

First—Obtain approximate titration indices by the method described above.

Second—Plot these indices against the square root of the ionic strength ($\sqrt{\mu}$) and draw straight line curves through the data for each index (below 0.1μ)⁷.

Third—At the value of $\sqrt{\mu}$ of each experimental point in the buffer range of a given titration index (say P_{G_1}') obtain a tentative value of the other index (P_{G_1}') from its curve in the above plot.

Fourth—With this series of P_{G_1}' values calculate the P_{G_1}' values by the procedure in Section II and plot them on the above plot and draw a line through the revised value of P_{G_1}' .

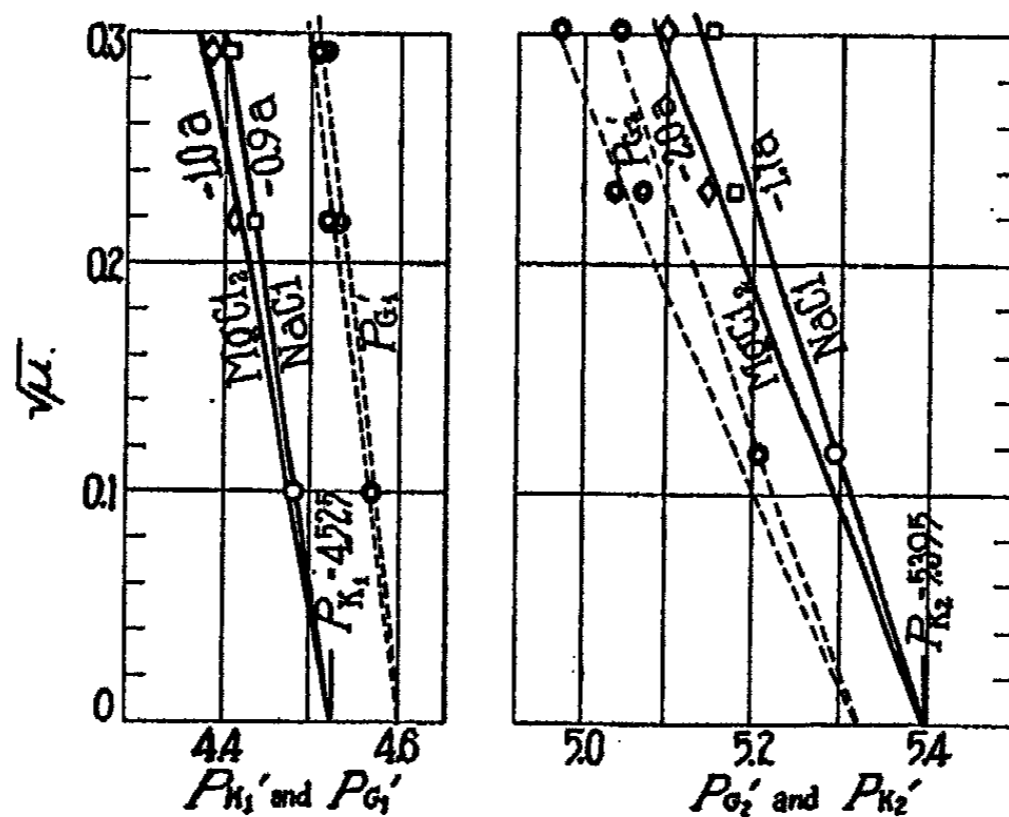


FIG. 5
Azelaic Acid
(The points represent average values).

Fifth—Obtain P_{G_1}' values from this line at the values of $\sqrt{\mu}$ of the points in the lower buffer range; calculate P_{G_1}' values from these; plot them and draw a line through them.

Sixth—If the above curves are satisfactory, obtain from them the values of $P_{G_1}' - P_{G_1}'$ at the $\sqrt{\mu}$ of each point. From these the values of $P_{G_1}' - P_{K_1}'$ (or $P_{K_1}' - P_{G_1}'$) may be obtained from the lower curve (extended if necessary) of Fig. 2 of the first paper.³ These when subtracted (or added) to P_{G_1}' (or P_{G_1}') give P_{K_1}' (or P_{K_1}').

Seventh—The dissociation indices (P_{K_1}' and P_{K_2}') when plotted against $\sqrt{\mu}$ should give straight line curves with slopes agreeing with those presented in this article.⁸

⁷ These curves should not be perfectly straight lines. If the dissociation indices (P_{K_1}') are a linear function of $\sqrt{\mu}$, the titration indices (P_{G_1}') will not be linear, since the relation between the dissociation and the titration indices is not linear.³ However there is little error in assuming the curves to be straight in dilute solution.

⁸ The last two steps may be performed on average P_{G_1}' values for points close together and the average P_{K_1}' values thus calculated may be plotted against average $\sqrt{\mu}$ values for these points.

The slopes indicate the extent of agreement or disagreement with the Debye-Hückel equation. The deviations observed in the data in this article are discussed in the previous article.

IV. Estimation of Ionic Strength

If a monovalent acid is titrated directly with strong base the ionic strength is given very closely by the equation:

$$\mu = b'c \quad (3)$$

The same formula applies to P_{G_1}' of an "isolated" polyvalent acid ($b' < 1.0$).

Between $b' = 1$ and $b' = 2$ of an isolated polyvalent acid the ion concentrations and values of $i\nu^2$ are as follows:

| | | |
|------------------------------|-----------|----------------------|
| $\text{Na}^+ + \text{H}^+ =$ | $b'c$ | $b'c$ |
| $\text{HA}^- =$ | $(2-b')c$ | $(2-b')c$ |
| $\text{HA}^- =$ | $(b'-1)c$ | $(2b'-2^2)c$ |
| $\text{Total} = 2\mu =$ | | $[2^2b' - (2^2-2)]c$ |

Hence in this range of b' :

$$\mu = \frac{2^2b' - (2^2 - 2)}{2} c \quad (4)$$

and in the special case of a very short acid where $2^2 = 4$ we get:

$$\mu = (2b' - 1)c \quad (4a)$$

Between $b' = 2$ and $b' = 3$ we find:

| | | |
|------------------------------|-----------|------------------------------------------------|
| $\text{Na}^+ + \text{H}^+ =$ | $b'c$ | $b'c$ |
| $\text{HA}^- =$ | $(3-b')c$ | $(3 \cdot 2^2 - 2^2b')c$ |
| $\text{A}^{2-} =$ | $(b'-2)c$ | $(3^2b' - 2 \cdot 3^2)c$ |
| $\text{Total} = 2\mu =$ | | $[(1+3^2-2^2) + (3 \cdot 2^2 - 2 \cdot 3^2)]c$ |

Hence in this range of b'

$$\mu = \frac{(1 + 3^2 - 2^2) + 3 \cdot 2^2 - 2 \cdot 3^2}{2} c \quad (5)$$

and in the very short acid where $2^2 = 4$ and $3^2 = 9$ we get:

$$\mu = 3(b' - 1)c \quad (5a)$$

In the presence of salt, the value of μ of the salt must be added to the above values to obtain total μ of the solution.

The above equations are correct only for acids with *isolated* constants. We are here interested in those with *overlapping* constants. For a correct calculation of the concentrations of the various ionic species we would need to use the equations for a divalent acid.

$$u = (1 - \alpha_1)(1 - \alpha_2) = \frac{H^2}{(H + G_1')(H + G_2')} \quad (6)$$

$$m = \alpha_1(1 - \alpha_2) + \alpha_2(1 - \alpha_1) = \frac{H(G_1' + G_2')}{(H + G_1')(H + G_2')} \quad (7)$$

$$d = \alpha_1\alpha_2 = \frac{G_1'G_2'}{(H + G_1')(H + G_2')} \quad (8)$$

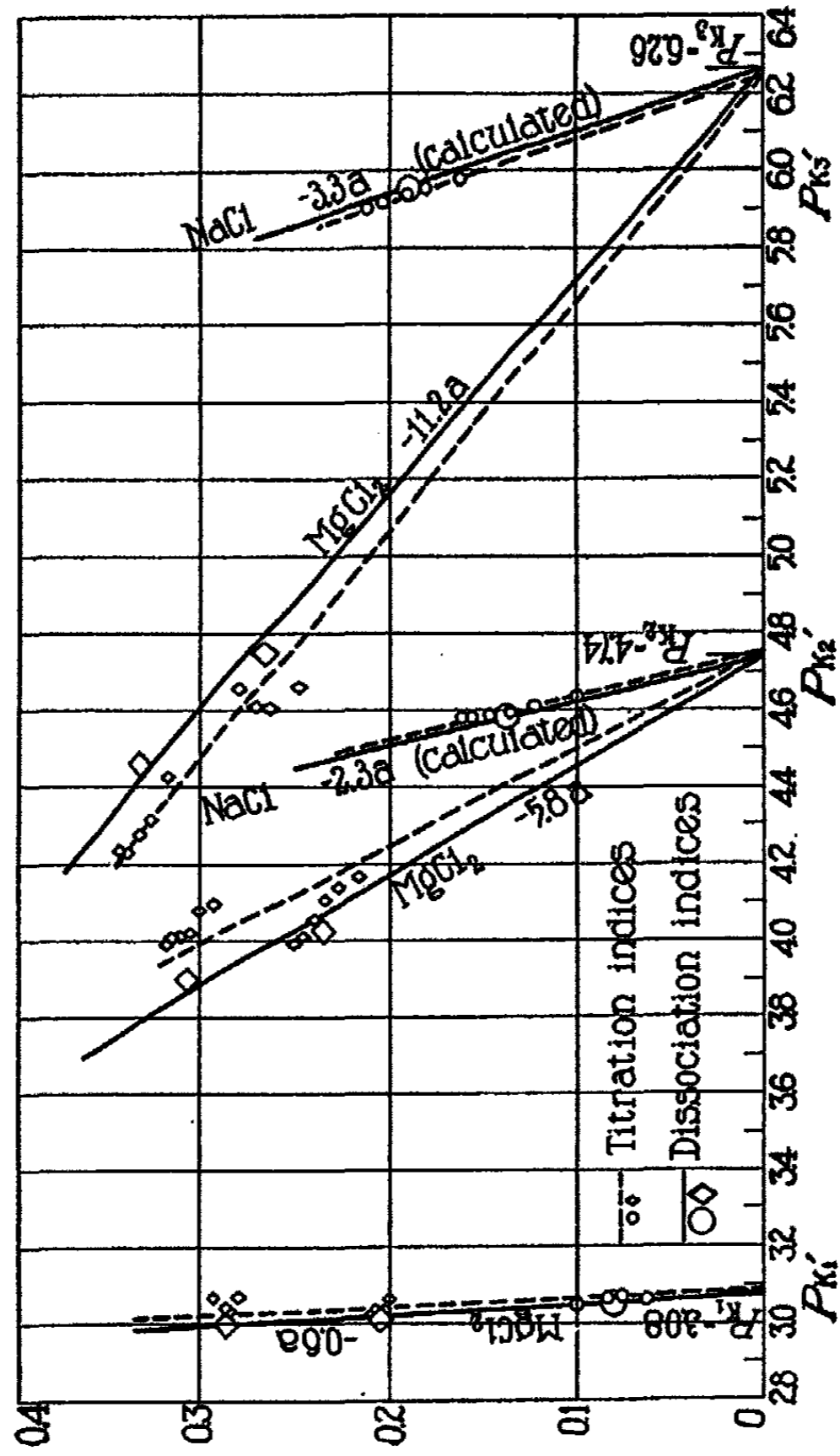


FIG. 6
Citric Acid

and similar equations for higher acids. However, this would be very complicated. Fortunately it is unnecessary since in this particular case it will not cause appreciable error to assume⁹ that $\mu = 1 - \alpha_1 - \alpha_2$, that $m = \alpha_1$, and that $d = \alpha_2$.

As examples of the use of Equations 4 and 5, azelaic acid ($r_d = 12.1 \text{ \AA}$) has a value of $z^s = 2.6$, hence μ between $b' = 1$ and 2 equals $(1.3 b' - 0.3)c$. Citric acid (mean $r_d = 7.4$) has values of $z^s = 3.25$ and $z^s = 6.5$; hence μ between $b' = 1$ and 2 equals $(1.6 b' - 0.6)c$, and between $b' = 2$ and 3 the value of μ is $(2.1 b' - 1.6)c$.

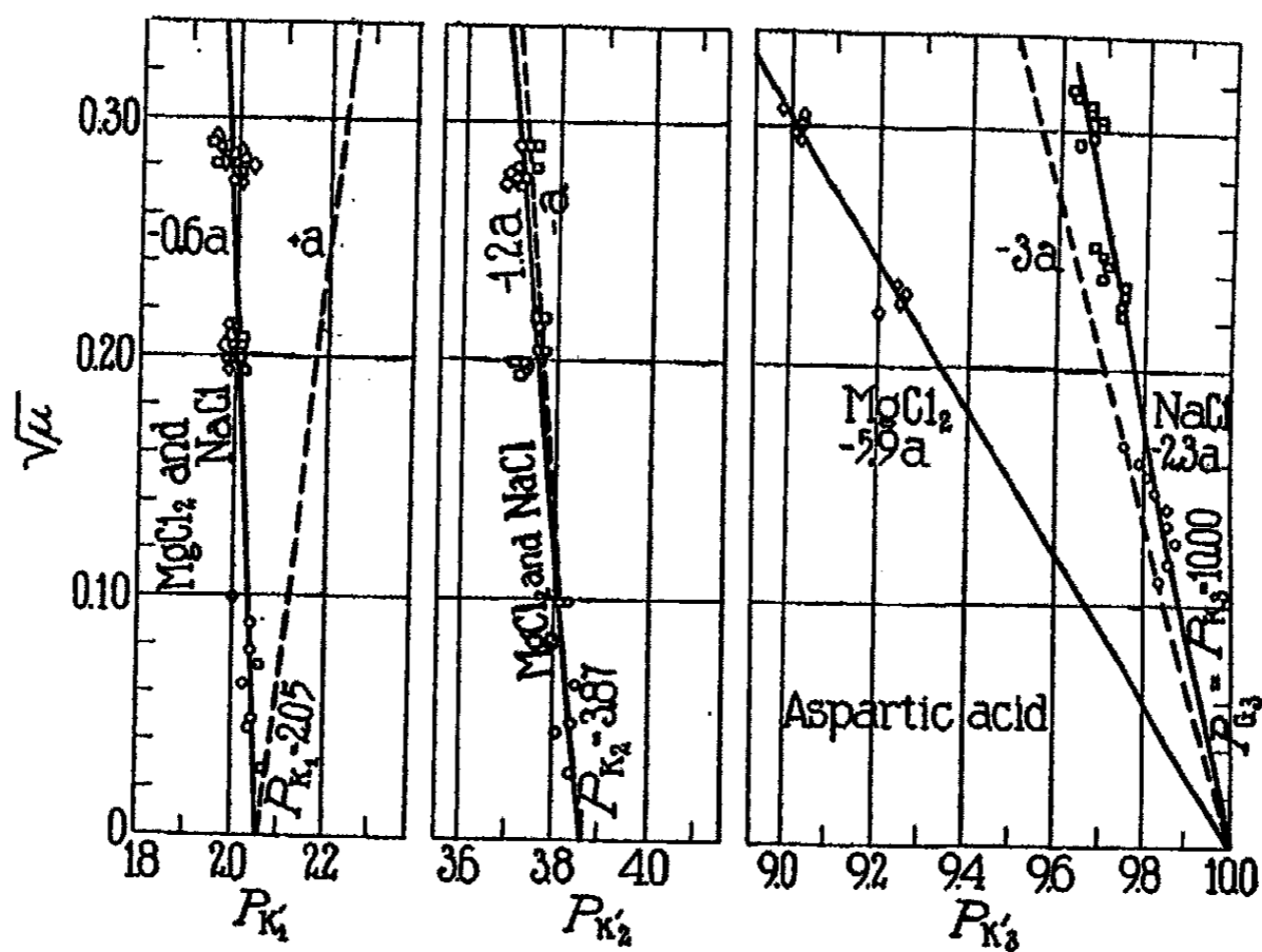


FIG. 7
Aspartic acid. The isoelectric point ($P_1 = 2.96$) has a slope of $-0.9a$ with either NaCl or MgCl_2 .

V. Experimental

The experimental conditions were described in the preceding paper. The data are presented in Tables I to VI and are plotted in Figs. 2 to 7.

The titration curve of citric acid without salt and in the presence of MgCl_2 is given in Fig. 1 to illustrate the extent of the effect of salts. The dotted curve is that calculated for the hypothetical case of zero ionic strength (infinite dilution).

It will be observed that malonic acid was titrated also in the presence of MgSO_4 and K_2SO_4 . The dilute and concentrated solutions have the same respective ionic strengths as those of NaCl and MgCl_2 .

The measurements reported in this and the preceding paper were made by Miss Virginia Rowland.

⁹ In dealing with any property of one ionic species, however, this assumption would be quite incorrect.

TABLE I A
Oxalic Acid (0.0500 molar)

| Salt | P_H | $\frac{b-a}{c}$ | b' | P_{G_1}' | $\sqrt{\mu}$ |
|-----------------------|-------|-----------------|-------|------------|--------------|
| C. -MgCl ₂ | 1.321 | -0.400 | 0.696 | 0.960 | 0.355 |
| D. -MgCl ₂ | 1.332 | -.400 | .668 | 1.082 | .297 |
| No salt | 1.343 | -.400 | .664 | 1.046 | .226 |
| D. -NaCl | 1.335 | -.400 | .662 | 1.042 | .297 |
| C. -NaCl | 1.323 | -.400 | .692 | 0.971 | .355 |
| C. -MgCl ₂ | 1.394 | -.200 | .727 | .968 | .342 |
| D. -MgCl ₂ | 1.403 | -.200 | .708 | 1.017 | .282 |
| No salt | 1.418 | -.200 | .676 | 1.098 | .205 |
| D. -NaCl | 1.408 | -.200 | .697 | 1.045 | .282 |
| C. -NaCl | 1.394 | -.200 | .727 | 1.068 | .342 |
| No salt | 1.502 | 0 | .722 | 1.087 | .178 |
| C. -MgCl ₂ | 1.565 | 0.200 | .826 | 0.888 | .336 |
| D. -MgCl ₂ | 1.585 | .200 | .796 | .994 | .273 |
| No salt | 1.606 | .200 | .768 | 1.085 | .193 |
| D. -NaCl | 1.590 | .200 | .790 | 1.014 | .273 |
| C. -NaCl | 1.582 | .200 | .802 | 0.975 | .336 |

TABLE I B
Oxalic Acid (0.00953 molar)

| Salt | P_H | $\frac{b-a}{c}$ | b' | P_{G_1}' | $\sqrt{\mu}$ |
|-----------------------|-------|-----------------|-------|------------|--------------|
| C. -MgCl ₂ | 2.513 | 0.944 | 1.314 | 2.853 | 0.292 |
| D. -MgCl ₂ | 2.618 | .944 | 1.228 | 3.148 | .218 |
| No salt | 2.961 | .944 | 1.070 | 4.086 | .101 |
| D. -NaCl | 2.925 | .944 | 1.084 | 3.965 | .218 |
| C. -NaCl | 2.885 | .944 | 1.102 | 3.831 | .292 |
| No salt | 3.210 | 1.048 | 1.121 | 4.072 | .104 |
| C. -MgCl ₂ | 2.682 | 1.154 | 1.410 | 2.841 | .295 |
| D. -MgCl ₂ | 2.837 | 1.154 | 1.330 | 3.145 | .223 |
| No salt | 3.445 | 1.154 | 1.195 | 4.061 | .115 |
| D. -NaCl | 3.345 | 1.154 | 1.209 | 3.924 | .223 |
| C. -NaCl | 3.277 | 1.154 | 1.219 | 3.829 | .295 |
| C. -MgCl ₂ | 2.782 | 1.258 | 1.463 | 2.846 | .298 |
| D. -MgCl ₂ | 2.971 | 1.258 | 1.391 | 3.164 | .227 |
| No salt | 3.671 | 1.258 | 1.283 | 4.076 | .127 |
| D. -NaCl | 3.553 | 1.258 | 1.294 | 3.934 | .227 |
| C. -NaCl | 3.468 | 1.258 | 1.301 | 3.835 | .298 |
| C. -MgCl ₂ | 2.902 | 1.364 | 1.518 | 2.871 | .302 |
| D. -MgCl ₂ | 3.113 | 1.364 | 1.460 | 3.182 | .231 |
| No salt | 3.853 | 1.364 | 1.381 | 4.064 | .130 |
| D. -NaCl | 3.734 | 1.364 | 1.387 | 3.934 | .231 |
| C. -NaCl | 3.634 | 1.364 | 1.392 | 3.825 | .302 |

TABLE I B (Continued)
Oxalic Acid (0.00953 molar)

| Salt | P_H | $\frac{b-a}{c}$ | b' | P_{G_1}' | $\sqrt{\mu}$ |
|------------------------|-------|-----------------|-------|------------|--------------|
| C. - MgCl ₂ | 3.044 | 1.468 | 1.580 | 2.903 | .305 |
| D. - MgCl ₂ | 3.292 | 1.468 | 1.532 | 3.237 | .236 |
| No salt | 4.024 | 1.468 | 1.481 | 4.057 | .137 |
| D. - NaCl | 3.908 | 1.468 | 1.485 | 3.934 | .236 |
| C. - NaCl | 3.829 | 1.468 | 1.487 | 3.850 | .305 |
| C. - MgCl ₂ | 3.182 | 1.574 | 1.655 | 2.903 | .308 |
| D. - MgCl ₂ | 3.479 | 1.574 | 1.615 | 3.275 | .240 |
| No salt | 4.201 | 1.574 | 1.581 | 4.058 | .143 |
| D. - NaCl | 4.078 | 1.574 | 1.584 | 3.930 | .240 |
| C. - NaCl | 4.005 | 1.574 | 1.587 | 3.851 | .308 |
| C. - MgCl ₂ | 3.353 | 1.678 | 1.734 | 2.912 | .312 |
| D. - MgCl ₂ | 3.683 | 1.678 | 1.704 | 3.306 | .244 |
| No salt | 4.387 | 1.678 | 1.684 | 4.051 | .150 |
| D. - NaCl | 4.269 | 1.678 | 1.685 | 3.931 | .244 |
| C. - NaCl | 4.191 | 1.678 | 1.687 | 3.849 | .312 |
| C. - MgCl ₂ | 3.585 | 1.784 | 1.816 | 2.937 | .315 |
| D. - MgCl ₂ | 3.949 | 1.784 | 1.798 | 3.353 | .248 |
| No salt | 4.616 | 1.784 | 1.787 | 4.048 | .157 |
| D. - NaCl | 4.504 | 1.784 | 1.788 | 3.933 | .248 |
| C. - NaCl | 4.431 | 1.784 | 1.788 | 3.860 | .315 |
| No salt | 10.6 | 2.098 | 1.94 | | |

TABLE II A

Malonic Acid (0.0100 molar)

Titrated not only with NaCl and MgCl₂ but also with K₂SO₄ and MgSO₄

| Salt | P_H | $\frac{b-a}{c}$ | b' | Estimated | | | P_{G_1}' | $\sqrt{\mu}$ |
|-------------------------------------|-------|-----------------|-------|------------|------------|------------|------------|--------------|
| | | | | P_{G_2}' | α_2 | α_1 | | |
| No salt | 2.506 | 0 | 0.312 | 5.670 | 0.001 | 0.311 | 2.852 | 0.056 |
| No salt | 2.782 | 0.300 | .469 | 5.657 | .001 | .468 | 2.837 | .068 |
| D. - MgCl ₂ | 2.760 | .300 | .499 | 5.184 | .004 | .495 | 2.769 | .205 |
| C. - MgCl ₂ | 2.738 | .300 | .515 | 4.975 | .006 | .509 | 2.723 | .282 |
| D. - NaCl | 2.761 | .300 | .499 | 5.495 | .002 | .497 | 2.766 | .205 |
| C. - NaCl | 2.743 | .300 | .512 | 5.405 | .002 | .510 | 2.726 | .282 |
| D. - MgSO ₄ | 2.800 | .300 | .482 | 5.275 | .003 | .479 | 2.836 | .205 |
| C. - MgSO ₄ | 2.842 | .300 | .469 | 5.100 | .006 | .463 | 2.906 | .282 |
| D. - K ₂ SO ₄ | 2.858 | .300 | .459 | 5.530 | .002 | .457 | 2.933 | .205 |
| C. - K ₂ SO ₄ | 2.897 | .300 | .449 | 5.454 | .003 | .446 | 2.991 | .282 |
| No salt | 2.788 | .300 | .467 | 5.657 | .001 | .466 | 2.847 | .068 |
| No salt | 3.049 | .500 | .594 | 5.646 | .002 | .592 | 2.888 | .077 |
| D. - MgCl ₂ | 2.976 | .500 | .621 | 5.175 | .006 | .615 | 2.773 | .208 |
| C. - MgCl ₂ | 2.944 | .500 | .634 | 4.969 | .009 | .625 | 2.722 | .284 |
| D. - NaCl | 2.978 | .500 | .621 | 5.491 | .003 | .618 | 2.769 | .208 |
| C. - NaCl | 2.958 | .500 | .629 | 5.402 | .004 | .625 | 2.736 | .284 |
| D. - MgSO ₄ | 3.030 | .500 | .607 | 5.268 | .006 | .601 | 2.852 | .208 |
| C. - MgSO ₄ | 3.042 | .500 | .607 | 5.096 | .009 | .598 | 2.870 | .284 |
| D. - K ₂ SO ₄ | 3.059 | .500 | .600 | 5.527 | .003 | .597 | 2.888 | .208 |
| C. - K ₂ SO ₄ | 3.093 | .500 | .595 | 5.452 | .004 | .591 | 2.933 | .284 |
| No salt | 3.015 | .500 | .601 | 5.646 | .002 | .599 | 2.841 | .077 |

TABLE II A (Continued)

| Salt | P_H | $\frac{b-a}{c}$ | b' | P_{G_1}' | α_1 | α_2 | P_{G_1}' | $\sqrt{\mu}$ |
|-------------------------------------|-------|-----------------|------|------------|------------|------------|------------|--------------|
| No salt | 3.338 | .700 | .749 | 5.634 | .005 | .744 | 2.875 | .087 |
| D. - MgCl ₂ | 3.274 | .700 | .760 | 5.164 | .013 | .747 | 2.804 | .212 |
| C. - MgCl ₂ | 3.233 | .700 | .769 | 4.962 | .018 | .751 | 2.754 | .287 |
| D. - NaCl | 3.293 | .700 | .758 | 5.487 | .006 | .752 | 2.812 | .212 |
| C. - NaCl | 3.266 | .700 | .764 | 5.399 | .012 | .752 | 2.785 | .287 |
| D. - MgSO ₄ | 3.337 | .700 | .753 | 5.259 | .012 | .741 | 2.881 | .212 |
| C. - MgSO ₄ | 3.323 | .700 | .756 | 5.090 | .017 | .739 | 2.871 | .287 |
| D. - K ₂ SO ₄ | 3.372 | .700 | .749 | 5.523 | .007 | .742 | 2.913 | .212 |
| C. - K ₂ SO ₄ | 3.387 | .700 | .748 | 5.449 | .009 | .739 | 2.935 | .287 |
| No salt | 3.350 | .700 | .748 | 5.634 | .005 | .743 | 2.889 | .087 |

TABLE II B
Malonic Acid (0.0100 molar)

| Salt | P_H | $\frac{b-a}{c}$ | b' | Estimated P_{G_1}' | α_1 | α_2 | P_{G_1}' | $\sqrt{\mu}$ |
|-------------------------------------|-------|-----------------|-------|----------------------|------------|------------|------------|--------------|
| No salt | 4.460 | 1.100 | 1.004 | | | | | |
| No salt | 5.201 | 1.300 | 1.301 | 2.823 | 0.996 | 0.305 | 5.559 | 0.126 |
| D. - MgCl ₂ | 4.748 | 1.300 | 1.302 | 2.744 | .990 | .312 | 5.092 | .231 |
| C. - MgCl ₂ | 4.482 | 1.300 | 1.304 | 2.699 | .984 | .320 | 4.809 | .302 |
| D. - NaCl | 5.100 | 1.300 | 1.301 | 2.766 | .995 | .306 | 5.456 | .231 |
| C. - NaCl | 5.022 | 1.300 | 1.301 | 2.728 | .995 | .306 | 5.378 | .302 |
| D. - MgSO ₄ | 4.836 | 1.300 | 1.302 | 2.845 | .990 | .312 | 5.180 | .231 |
| C. - MgSO ₄ | 4.670 | 1.300 | 1.303 | 2.830 | .986 | .317 | 5.003 | .302 |
| D. - K ₂ SO ₄ | 5.135 | 1.300 | 1.301 | 2.910 | .994 | .307 | 5.489 | .231 |
| C. - K ₂ SO ₄ | 5.083 | 1.300 | 1.301 | 2.915 | .993 | .308 | 5.435 | .302 |
| No salt | 5.231 | 1.300 | 1.301 | 2.823 | .996 | .305 | 5.589 | .126 |
| No salt | 5.563 | 1.500 | 1.500 | 2.815 | .998 | .502 | 5.560 | .141 |
| D. - MgCl ₂ | 5.118 | 1.500 | 1.501 | 2.739 | .996 | .505 | 5.109 | .240 |
| C. - MgCl ₂ | 4.864 | 1.500 | 1.502 | 2.695 | .993 | .509 | 4.848 | .308 |
| D. - NaCl | 5.436 | 1.500 | 1.500 | 2.762 | .998 | .502 | 5.433 | .240 |
| C. - NaCl | 5.364 | 1.500 | 1.501 | 2.725 | .998 | .503 | 5.359 | .308 |
| D. - MgSO ₄ | 5.208 | 1.500 | 1.501 | 2.844 | .996 | .505 | 5.199 | .240 |
| C. - MgSO ₄ | 5.025 | 1.500 | 1.501 | 2.830 | .994 | .507 | 5.013 | .308 |
| D. - K ₂ SO ₄ | 5.485 | 1.500 | 1.500 | 2.911 | .997 | .503 | 5.480 | .240 |
| C. - K ₂ SO ₄ | 5.430 | 1.500 | 1.500 | 2.916 | .997 | .503 | 5.425 | .308 |
| No salt | 5.570 | 1.500 | 1.500 | 2.815 | .998 | .502 | 5.567 | .141 |
| No salt | 5.924 | 1.700 | 1.700 | 2.807 | .999 | .701 | 5.553 | .155 |
| D. - MgCl ₂ | 5.538 | 1.700 | 1.700 | 2.734 | .998 | .702 | 5.165 | .248 |
| C. - MgCl ₂ | 5.260 | 1.700 | 1.701 | 2.692 | .997 | .704 | 4.883 | .315 |
| D. - NaCl | 5.814 | 1.700 | 1.700 | 2.756 | .999 | .701 | 5.443 | .248 |
| C. - NaCl | 5.738 | 1.700 | 1.700 | 2.721 | .999 | .701 | 5.367 | .315 |
| D. - MgSO ₄ | 5.599 | 1.700 | 1.700 | 2.841 | .998 | .702 | 5.226 | .248 |
| C. - MgSO ₄ | 5.424 | 1.700 | 1.700 | 2.828 | .998 | .702 | 5.051 | .315 |
| D. - K ₂ SO ₄ | 5.846 | 1.700 | 1.700 | 2.911 | .999 | .701 | 5.475 | .248 |
| C. - K ₂ SO ₄ | 5.804 | 1.700 | 1.700 | 2.916 | .999 | .701 | 5.433 | .315 |
| No salt | 5.924 | 1.700 | 1.700 | 2.807 | .999 | .701 | 5.553 | .155 |
| No salt | 8.8 | 2.000 | 2.000 | | | | | |

TABLE III A
 Succinic Acid (0.00984 molar)

| Salt | P_H | $\frac{b-a}{c}$ | b' | Estimated | | α_1 | P_{G_1}' | $\sqrt{\mu}$ |
|------------------------|-------|-----------------|-------|------------|------------|------------|------------|--------------|
| | | | | P_{G_1}' | α_2 | | | |
| C. - MgCl ₂ | 3.044 | 0 | 0.108 | 5.190 | 0.007 | 0.101 | (3.994) | 0.274 |
| D. - MgCl ₂ | 3.064 | 0 | .101 | 5.305 | .006 | .095 | (4.042) | .194 |
| No salt | 3.091 | 0 | .082 | 5.540 | .004 | .078 | 4.165 | .028 |
| D. - NaCl | 3.061 | 0 | .101 | 5.350 | .005 | .096 | 4.034 | .194 |
| C. - NaCl | 3.051 | 0 | .108 | 5.260 | .006 | .102 | 3.996 | .274 |
| C. - MgCl ₂ | 3.501 | 0.203 | .241 | 5.185 | .019 | .222 | 4.046 | .377 |
| D. - MgCl ₂ | 3.541 | .203 | .237 | 5.295 | .016 | .221 | 4.088 | .199 |
| No salt | 3.609 | .203 | .229 | 5.515 | .012 | .217 | 4.167 | .047 |
| D. - NaCl | 3.541 | .203 | .237 | 5.345 | .014 | .223 | 4.083 | .199 |
| C. - NaCl | 3.511 | .203 | .241 | 5.255 | .016 | .225 | 4.048 | .277 |
| C. - MgCl ₂ | 3.842 | .406 | .424 | 5.180 | .044 | .380 | 4.055 | .281 |
| D. - MgCl ₂ | 3.895 | .406 | .422 | 5.290 | .039 | .383 | 4.102 | .204 |
| No salt | 3.984 | .406 | .418 | 5.495 | .028 | .390 | 4.179 | .064 |
| D. - NaCl | 3.902 | .406 | .422 | 5.430 | .033 | .389 | 4.098 | .204 |
| C. - NaCl | 3.863 | .406 | .424 | 5.250 | .040 | .384 | 4.069 | .281 |
| C. - MgCl ₂ | 4.120 | .609 | .619 | 5.175 | .081 | .538 | 4.054 | .285 |
| D. - MgCl ₂ | 4.171 | .609 | .618 | 5.285 | .071 | .547 | 4.089 | .208 |
| No salt | 4.271 | .609 | .616 | 5.480 | .059 | .557 | 4.171 | .078 |
| D. - NaCl | 4.179 | .609 | .618 | 5.335 | .065 | .553 | 4.086 | .208 |
| C. - NaCl | 4.137 | .609 | .619 | 5.250 | .072 | .547 | 4.055 | .285 |
| C. - MgCl ₂ | 4.379 | .812 | .818 | 5.170 | .139 | .679 | 4.053 | .288 |
| D. - MgCl ₂ | 4.434 | .812 | .817 | 5.275 | .126 | .691 | 4.084 | .213 |
| No salt | 4.545 | .812 | .816 | 5.470 | .106 | .710 | 4.155 | .090 |
| D. - NaCl | 4.450 | .812 | .817 | 5.330 | .117 | .700 | 4.081 | .213 |
| C. - NaCl | 4.404 | .812 | .818 | 5.245 | .126 | .692 | 4.052 | .288 |
| C. - MgCl ₂ | 4.606 | 1.016 | 1.018 | 5.165 | .217 | .801 | (4.001) | .292 |
| D. - MgCl ₂ | 4.685 | 1.016 | 1.018 | 5.270 | .206 | .812 | (4.049) | .218 |
| No salt | 4.829 | 1.016 | 1.118 | 5.455 | .191 | .827 | 4.149 | .100 |
| D. - NaCl | 4.710 | 1.106 | 1.018 | 5.325 | .195 | .823 | 4.042 | .218 |
| C. - NaCl | 4.663 | 1.016 | 1.018 | 5.240 | .210 | .808 | 4.039 | .292 |

 TABLE III B
 Succinic Acid (0.00984 molar)

| Salt | P_H | $\frac{b-a}{c}$ | b' | Estimated | | α_2 | P_{G_2}' | $\sqrt{\mu}$ |
|------------------------|-------|-----------------|-------|------------|------------|------------|------------|--------------|
| | | | | P_{G_1}' | α_1 | | | |
| C. - MgCl ₂ | 4.606 | 1.016 | 1.018 | 4.040 | 0.786 | 0.232 | 5.127 | 0.292 |
| D. - MgCl ₂ | 4.685 | 1.016 | 1.018 | 4.080 | .801 | .217 | 5.242 | .218 |
| No salt | 4.829 | 1.016 | 1.018 | 4.140 | .830 | .188 | 5.465 | .100 |
| D. - NaCl | 4.710 | 1.016 | 1.018 | 4.080 | .813 | .205 | 5.299 | .218 |
| C. - NaCl | 4.663 | 1.016 | 1.018 | 4.045 | .806 | .212 | 5.234 | .292 |
| C. - MgCl ₂ | 4.736 | 1.117 | 1.119 | 4.040 | .832 | .287 | 5.132 | .295 |
| D. - MgCl ₂ | 4.819 | 1.117 | 1.119 | 4.075 | .847 | .272 | 5.247 | .223 |
| No salt | 4.954 | 1.117 | 1.118 | 4.135 | .868 | .250 | 5.431 | .110 |
| D. - NaCl | 4.848 | 1.117 | 1.119 | 4.080 | .854 | .265 | 5.291 | .223 |
| C. - NaCl | 4.797 | 1.117 | 1.119 | 4.040 | .851 | .268 | 5.233 | .295 |

TABLE III B (Continued)

| Salt | P_H | $\frac{b-a}{c}$ | b' | P_{G_1}' | α_1 | α_2 | P_{G_2}' | $\sqrt{\mu}$ |
|------------------------|-------|-----------------|-------|------------|------------|------------|------------|--------------|
| C. - MgCl ₂ | 4.998 | 1.320 | 1.322 | 4.040 | .901 | .421 | 5.137 | .302 |
| D. - MgCl ₂ | 5.088 | 1.320 | 1.322 | 4.075 | .911 | .411 | 5.245 | .231 |
| No salt | 5.237 | 1.320 | 1.322 | 4.125 | .928 | .394 | 5.424 | .127 |
| D. - NaCl | 5.125 | 1.320 | 1.322 | 4.075 | .918 | .404 | 5.294 | .231 |
| C. - NaCl | 5.073 | 1.320 | 1.322 | 4.040 | .915 | .407 | 5.237 | .302 |
| C. - MgCl ₂ | 5.277 | 1.523 | 1.524 | 4.035 | .946 | .578 | 5.140 | .308 |
| D. - MgCl ₂ | 5.375 | 1.523 | 1.523 | 4.070 | .953 | .570 | 5.252 | .240 |
| No salt | 5.523 | 1.523 | 1.523 | 4.120 | .962 | .561 | 5.416 | .141 |
| D. - NaCl | 5.409 | 1.523 | 1.523 | 4.070 | .956 | .567 | 5.291 | .240 |
| C. - NaCl | 5.353 | 1.523 | 1.524 | 4.035 | .954 | .570 | 5.230 | .308 |
| C. - MgCl ₂ | 5.441 | 1.625 | 1.625 | 4.035 | .962 | .663 | 5.146 | .312 |
| D. - MgCl ₂ | 5.539 | 1.625 | 1.625 | 4.065 | .967 | .658 | 5.254 | .244 |
| No salt | 5.685 | 1.625 | 1.625 | 4.115 | .974 | .651 | 5.414 | .148 |
| D. - NaCl | 5.577 | 1.625 | 1.625 | 4.065 | .970 | .655 | 5.298 | .244 |
| C. - NaCl | 5.521 | 1.625 | 1.625 | 4.035 | .968 | .657 | 5.238 | .312 |
| C. - MgCl ₂ | 5.622 | 1.726 | 1.727 | 4.030 | .976 | .751 | 5.142 | .315 |
| D. - MgCl ₂ | 5.719 | 1.726 | 1.727 | 4.065 | .979 | .748 | 5.247 | .248 |
| No Salt | 5.866 | 1.726 | 1.727 | 4.110 | .983 | .744 | 5.403 | .155 |
| D. - NaCl | 5.756 | 1.726 | 1.727 | 4.065 | .980 | .747 | 5.286 | .248 |
| C. - NaCl | 5.698 | 1.726 | 1.727 | 4.030 | .980 | .747 | 5.228 | .315 |
| C. - MgCl ₂ | 5.861 | 1.828 | 1.828 | 4.030 | .986 | .842 | 5.133 | .318 |
| D. - MgCl ₂ | 5.964 | 1.828 | 1.828 | 4.060 | .988 | .840 | 5.242 | .252 |
| No salt | 6.100 | 1.828 | 1.828 | 4.110 | .990 | .838 | 5.385 | .161 |
| D. - NaCl | 5.995 | 1.828 | 1.828 | 4.060 | .988 | .840 | 5.273 | .252 |
| C. - NaCl | 5.935 | 1.828 | 1.828 | 4.030 | .988 | .840 | 5.213 | .318 |
| C. - MgCl ₂ | 6.208 | 1.930 | 1.930 | 4.030 | .993 | .937 | (5.034) | .321 |
| D. - MgCl ₂ | 6.301 | 1.930 | 1.930 | 4.060 | .994 | .936 | (5.136) | .256 |
| No salt | 6.507 | 1.930 | 1.930 | 4.105 | .995 | .935 | 5.347 | .167 |
| D. - NaCl | 6.304 | 1.930 | 1.930 | 4.060 | .994 | .936 | 5.139 | .256 |
| C. - NaCl | 6.264 | 1.930 | 1.930 | 4.030 | .994 | .936 | 5.099 | .321 |
| No Salt | 8.0 | 2.031 | | | | | | |

TABLE IV A

Azelaic Acid (0.0100 molar, 1 equivalent of base added to mother solution)

| Salt | P_H | $\frac{b-a}{c}$ | b' | Estimated P_{G_1}' | α_2 | α_1 | P_{G_1}' | $\sqrt{\mu}$ |
|------------------------|-------|-----------------|-------|----------------------|------------|------------|------------|--------------|
| C. - MgCl ₂ | 4.247 | 0.500 | 0.507 | 4.975 | 0.158 | 0.349 | 4.518 | 0.292 |
| D. - MgCl ₂ | 4.286 | .500 | .506 | 5.065 | .143 | .363 | 4.530 | .218 |
| No salt | 4.374 | .500 | .505 | 5.241 | .120 | .385 | 4.578 | .100 |
| D. - NaCl | 4.305 | .500 | .506 | 5.103 | .137 | .369 | 4.538 | .218 |
| C. - NaCl | 4.271 | .500 | .506 | 5.025 | .150 | .356 | 4.528 | .292 |
| C. - MgCl ₂ | 4.462 | .700 | .704 | 4.975 | .235 | .469 | 4.516 | .292 |
| D. - MgCl ₂ | 4.506 | .700 | .704 | 5.065 | .216 | .488 | 4.527 | .218 |
| No salt | 4.604 | .700 | .703 | 5.241 | .188 | .515 | 4.578 | .100 |
| D. - NaCl | 4.522 | .700 | .703 | 5.103 | .209 | .494 | 4.533 | .218 |
| C. - NaCl | 4.484 | .700 | .704 | 5.025 | .223 | .481 | 4.517 | .292 |
| C. - MgCl ₂ | 4.644 | .900 | .903 | 4.975 | .319 | .584 | 4.496 | .292 |
| D. - MgCl ₂ | 4.694 | .900 | .902 | 5.065 | .299 | .603 | 4.512 | .218 |
| No salt | 4.800 | .900 | .902 | 5.241 | .266 | .636 | 4.558 | .100 |
| D. - NaCl | 4.714 | .910 | .902 | 5.103 | .291 | .611 | 4.518 | .218 |
| C. - NaCl | 4.672 | .900 | .903 | 5.025 | .308 | .585 | 4.504 | .292 |

TABLE IV A (Continued)

| Salt | P_H | $\frac{b-a}{c}$ | b' | P_{G_2}' | α_2 | α_1 | P_{G_1}' | $\sqrt{\mu}$ |
|------------------------|-------|-----------------|-------|------------|------------|------------|------------|--------------|
| C. - MgCl ₂ | 4.739 | 1.000 | 1.002 | 4.975 | .367 | .635 | 4.499 | .292 |
| D. - MgCl ₂ | 4.787 | 1.000 | 1.002 | 5.065 | .346 | .656 | 4.506 | .218 |
| No salt | 4.902 | 1.000 | 1.001 | 5.241 | .314 | .687 | 4.560 | .100 |
| D. - NaCl | 4.816 | 1.000 | 1.002 | 5.103 | .341 | .661 | 4.526 | .218 |
| C. - NaCl | 4.772 | 1.000 | 1.002 | 5.025 | .358 | .644 | 4.515 | .292 |

TABLE IV B

Azelaic Acid (0.0100 molar, 1 equivalent of base added to mother solution)

| Salt | P_H | $\frac{b-a}{c}$ | b' | Estimated | | | P_{G_2}' | $\sqrt{\mu}$ |
|------------------------|-------|-----------------|-------|------------|------------|------------|------------|--------------|
| | | | | P_{G_1}' | α_1 | α_2 | | |
| C. - MgCl ₂ | 4.739 | 1.000 | 1.002 | 4.518 | 0.624 | 0.378 | 4.956 | 0.292 |
| D. - MgCl ₂ | 4.787 | 1.000 | 1.002 | 4.551 | .633 | .369 | 5.020 | .218 |
| No salt | 4.902 | 1.000 | 1.001 | 4.584 | .675 | .326 | 5.218 | .100 |
| D. - NaCl | 4.816 | 1.000 | 1.002 | 4.563 | .642 | .360 | 5.066 | .218 |
| C. - NaCl | 4.772 | 1.000 | 1.002 | 4.499 | .652 | .350 | 5.041 | .292 |
| C. - MgCl ₂ | 4.846 | 1.100 | 1.102 | 4.515 | .681 | .421 | 4.985 | .295 |
| D. - MgCl ₂ | 4.893 | 1.100 | 1.101 | 4.549 | .688 | .413 | 5.046 | .223 |
| No salt | 5.010 | 1.100 | 1.101 | 4.583 | .727 | .374 | 5.234 | .105 |
| D. - NaCl | 4.920 | 1.100 | 1.101 | 4.561 | .695 | .406 | 5.086 | .223 |
| C. - NaCl | 4.880 | 1.100 | 1.101 | 4.497 | .707 | .394 | 5.067 | .295 |
| C. - MgCl ₂ | 5.042 | 1.300 | 1.301 | 4.511 | .772 | .529 | 4.992 | .302 |
| D. - MgCl ₂ | 5.088 | 1.300 | 1.301 | 4.546 | .777 | .524 | 5.046 | .231 |
| No salt | 5.201 | 1.300 | 1.301 | 4.578 | .808 | .493 | 5.213 | .118 |
| D. - NaCl | 5.100 | 1.300 | 1.301 | 4.558 | .781 | .520 | 5.076 | .231 |
| C. - NaCl | 5.064 | 1.300 | 1.301 | 4.492 | .788 | .513 | 5.042 | .302 |
| C. - MgCl ₂ | 5.252 | 1.500 | 1.501 | 4.507 | .847 | .654 | 4.975 | .308 |
| D. - MgCl ₂ | 5.308 | 1.500 | 1.501 | 4.543 | .853 | .648 | 5.043 | .240 |
| No salt | 5.421 | 1.500 | 1.500 | 4.574 | .875 | .625 | 5.199 | .128 |
| D. - NaCl | 5.323 | 1.500 | 1.501 | 4.554 | .854 | .647 | 5.060 | .240 |
| C. - NaCl | 5.276 | 1.500 | 1.501 | 4.485 | .861 | .640 | 5.026 | .308 |
| C. - MgCl ₂ | 5.522 | 1.700 | 1.700 | 4.498 | .913 | .787 | 4.954 | .315 |
| D. - MgCl ₂ | 5.587 | 1.700 | 1.700 | 4.539 | .917 | .783 | 5.030 | .248 |
| No salt | 5.700 | 1.700 | 1.700 | 4.571 | .931 | .769 | 5.177 | .138 |
| D. - NaCl | 5.614 | 1.700 | 1.700 | 4.550 | .920 | .780 | 5.064 | .248 |
| C. - NaCl | 5.570 | 1.700 | 1.700 | 4.477 | .925 | .775 | 5.033 | .315 |

TABLE IV C

Azelaic Acid. Calculation of Dissociation Indices from Average Values

| Salt | P_{G_1}' | $P_{G_2}' - P_{G_1}'$ | $P_{G_1}' - P_{K_1}'$ | P_{K_1}' | $\sqrt{\mu}$ |
|------------------------|------------|-----------------------|-----------------------|------------|--------------|
| C. - MgCl ₂ | 4.507 | 0.48 | 0.121 | 4.386 | 0.292 |
| D. - MgCl ₂ | 4.519 | .54 | .108 | 4.411 | .218 |
| No salt | 4.568 | .66 | .085 | 4.483 | .100 |
| D. - NaCl | 4.529 | .58 | .099 | 4.430 | .218 |
| C. - NaCl | 4.516 | .53 | .110 | 4.406 | .292 |
| Salt | P_{G_2}' | $P_{G_2}' - P_{G_1}'$ | $P_{K_1}' - P_{G_2}'$ | P_{K_1}' | $\sqrt{\mu}$ |
| C. - MgCl ₂ | 4.972 | 0.46 | 0.128 | 5.100 | 0.302 |
| D. - MgCl ₂ | 5.037 | .51 | .110 | 5.147 | .232 |
| No salt | 5.208 | .65 | .086 | 5.294 | .118 |
| D. - NaCl | 5.070 | .54 | .108 | 5.178 | .232 |
| C. - NaCl | 5.042 | .53 | .110 | 5.152 | .302 |

TABLE V A
Citric Acid (0.0100 molar, 1 equivalent of base added to mother solution)

| Salt | pH | $\frac{b-a}{c}$ | b' | P _{G1} ' | Estimated | | | α ₁ | P _{G1} ' | √μ |
|------------------------|-------|-----------------|-------|-------------------|-------------------|----------------|----------------|----------------|-------------------|-------|
| | | | | | P _{G1} ' | α ₂ | α ₃ | | | |
| No salt | 2.594 | 0 | 0.225 | 4.688 | 6.156 | 0.008 | 0.000 | 0.217 | (3.152) | 0.055 |
| D. - MgCl ₂ | 2.574 | 0 | .267 | 4.266 | 5.070 | .020 | .003 | .244 | 3.065 | .200 |
| C. - MgCl ₂ | 2.560 | 0 | .275 | 4.071 | 4.600 | .030 | .009 | .236 | 3.070 | .279 |
| No salt | 2.904 | 0.300 | .425 | 4.670 | 6.144 | .017 | .001 | .407 | 3.067 | .063 |
| D. - MgCl ₂ | 2.854 | .300 | .440 | 4.258 | 5.053 | .038 | .006 | .396 | 3.037 | .203 |
| C. - MgCl ₂ | 2.821 | .300 | .451 | 4.063 | 4.580 | .054 | .017 | .380 | 3.034 | .283 |
| No salt | 3.145 | .500 | .572 | 4.663 | 6.121 | .030 | .001 | .541 | 3.074 | .077 |
| D. - MgCl ₂ | 3.064 | .500 | .586 | 4.248 | 5.026 | .061 | .011 | .514 | 3.040 | .207 |
| C. - MgCl ₂ | 3.017 | .500 | .596 | 4.058 | 4.566 | .083 | .028 | .485 | 3.043 | .285 |
| No salt | 3.404 | .700 | .739 | 4.656 | 6.110 | .053 | .002 | .684 | 3.069 | .084 |
| D. - MgCl ₂ | 3.272 | .700 | .753 | 4.241 | 5.010 | .097 | .018 | .638 | 3.026 | .210 |
| No salt | 3.859 | 1.000 | 1.014 | 4.636 | 6.084 | .143 | .006 | .865 | 3.051 | .100 |
| D. - MgCl ₂ | 3.584 | 1.000 | 1.026 | 4.224 | 4.967 | .186 | .040 | .800 | (2.982) | .217 |
| C. - MgCl ₂ | 3.492 | 1.000 | 1.032 | 4.040 | 4.526 | .221 | .085 | .726 | 3.069 | .292 |

TABLE V B
Citric Acid (0.0100 molar, 1 equivalent of base added to mother solution)

| Salt | pH | $\frac{b-a}{c}$ | b' | Estimated | | | α_2 | P _{G₂'} | $\sqrt{\mu}$ |
|------------------------|-------|-----------------|-------|-----------------------------|-----------------------------|------------|------------|-----------------------------|--------------|
| | | | | P _{G₁'} | P _{G₂'} | α_1 | | | |
| No salt | 3.859 | 1.000 | 1.014 | 3.056 | 6.084 | 0.864 | 0.006 | 4.634 | 0.100 |
| D. - MgCl ₂ | 3.584 | 1.000 | 1.026 | 3.040 | 4.968 | .778 | .040 | 4.165 | .217 |
| C. - MgCl ₂ | 3.492 | 1.000 | 1.032 | 3.023 | 4.526 | .747 | .085 | 4.094 | .292 |
| No salt | 4.320 | 1.300 | 1.305 | 3.047 | 6.048 | .949 | .018 | 4.612 | .122 |
| D. - MgCl ₂ | 3.876 | 1.300 | 1.313 | 3.038 | 4.903 | .873 | .086 | 4.137 | .228 |
| C. - MgCl ₂ | 3.746 | 1.300 | 1.318 | 3.021 | 4.479 | .842 | .156 | 4.073 | .300 |
| No salt | 4.589 | 1.500 | 1.503 | 3.041 | 6.028 | .972 | .035 | 4.596 | .134 |
| D. - MgCl ₂ | 4.046 | 1.500 | 1.509 | 3.036 | 4.860 | .911 | .133 | 4.107 | .235 |
| C. - MgCl ₂ | 3.881 | 1.500 | 1.513 | 3.020 | 4.448 | .879 | .213 | 4.019 | .305 |
| No salt | 4.854 | 1.700 | 1.701 | 3.036 | 6.010 | .985 | .065 | 4.583 | .145 |
| D. - MgCl ₂ | 4.196 | 1.700 | 1.706 | 3.035 | 4.825 | .936 | .190 | 4.056 | .241 |
| C. - MgCl ₂ | 4.030 | 1.700 | 1.709 | 3.019 | 4.420 | .911 | .290 | 4.016 | .310 |
| No salt | 5.144 | 1.900 | 1.901 | 3.031 | 5.994 | .992 | .124 | 4.581 | .155 |
| D. - MgCl ₂ | 4.347 | 1.900 | 1.904 | 3.034 | 4.789 | .954 | .265 | 4.010 | .247 |
| C. - MgCl ₂ | 4.173 | 1.900 | 1.907 | 3.018 | 4.387 | .935 | .379 | 4.010 | .315 |
| No salt | 5.291 | 2.000 | 2.001 | 3.029 | 5.983 | .995 | .169 | 4.580 | .161 |
| D. - MgCl ₂ | 4.423 | 2.000 | 2.004 | 3.032 | 4.765 | .961 | .313 | 3.991 | .251 |
| C. - MgCl ₂ | 4.238 | 2.000 | 2.006 | 3.017 | 4.373 | .943 | .423 | 3.988 | .318 |

TABLE V C
Citric Acid (0.0100 molar, 1 equivalent of base added to mother solution)

| Salt | P_H | $\frac{b-a}{c}$ | b' | P_{G_1}' | Estimated | | | α_3 | P_{G_1}' | $\sqrt{\mu}$ |
|------------------------|-------|-----------------|-------|------------|------------|------------|------------|------------|------------|--------------|
| | | | | | P_{G_1}' | α_1 | α_2 | | | |
| No salt | 5.291 | 2.000 | 2.001 | 3.029 | 4.581 | 0.995 | 0.837 | 0.169 | 5.983 | 0.161 |
| D. - MgCl ₂ | 4.423 | 2.000 | 2.004 | 2.988 | 4.133 | 0.964 | 0.671 | 0.369 | 4.656 | 0.251 |
| C. - MgCl ₂ | 4.238 | 2.000 | 2.006 | 3.017 | 3.937 | 0.943 | 0.667 | 0.396 | 4.422 | 0.318 |
| No salt | 5.716 | 2.300 | 2.300 | 3.020 | 4.561 | 0.998 | 0.935 | 0.367 | 5.953 | 0.179 |
| D. - MgCl ₂ | 4.660 | 2.300 | 2.302 | 2.982 | 4.081 | 0.979 | 0.791 | 0.532 | 4.605 | 0.263 |
| C. - MgCl ₂ | 4.438 | 2.300 | 2.304 | 3.015 | 3.914 | 0.964 | 0.770 | 0.570 | 4.310 | 0.327 |
| No salt | 6.000 | 2.500 | 2.500 | 3.016 | 4.549 | 0.999 | 0.966 | 0.535 | 5.939 | 0.190 |
| D. - MgCl ₂ | 4.873 | 2.500 | 2.501 | 2.980 | 4.063 | 0.987 | 0.866 | 0.648 | 4.608 | 0.270 |
| C. - MgCl ₂ | 4.616 | 2.500 | 2.502 | 3.014 | 3.898 | 0.975 | 0.839 | 0.688 | 4.272 | 0.333 |
| No salt | 6.321 | 2.700 | 2.700 | 3.010 | 4.534 | 1.000 | 0.984 | 0.716 | 5.919 | 0.203 |
| D. - MgCl ₂ | 5.189 | 2.700 | 2.701 | 2.974 | 4.039 | 0.994 | 0.934 | 0.773 | 4.657 | 0.279 |
| C. - MgCl ₂ | 4.858 | 2.700 | 2.701 | 3.011 | 3.878 | 0.986 | 0.905 | 0.810 | 4.229 | 0.341 |
| No salt | 6.874 | 2.900 | 2.900 | 3.005 | 4.524 | 1.000 | 0.996 | 0.904 | 5.901 | 0.212 |
| D. - MgCl ₂ | 5.831 | 2.900 | 2.900 | 2.972 | 4.021 | 0.999 | 0.985 | 0.916 | (4.794) | 0.286 |
| C. - MgCl ₂ | 5.370 | 2.900 | 2.900 | 3.010 | 3.864 | 0.996 | 0.970 | 0.934 | 4.232 | 0.346 |
| No salt | 7.78 | 3.000 | 3.000 | 3.002 | 4.518 | 1.000 | 0.999 | 1.001 | | 0.217 |
| D. - MgCl ₂ | 6.8 | 3.000 | 3.000 | 2.970 | 4.011 | 1.000 | 0.998 | 1.002 | | 0.290 |
| C. - MgCl ₂ | 6.6 | 3.000 | 3.000 | 3.010 | 3.856 | 1.000 | 0.998 | 1.002 | | 0.349 |

TABLE V D

Citric Acid.

Calculation of Dissociation Indices from average values, using equations
(I 16 - 19)

| Salt | $\sqrt{\mu_1}$ | $\sqrt{\mu_2}$ | $\sqrt{\mu_3}$ | P_{G_1}' | P_{G_2}' | P_{G_3}' | P_{K_1}' | P_{K_2}' | P_{K_3}' |
|------------------------|----------------|----------------|----------------|------------|------------|------------|------------|------------|------------|
| No salt | 0.081 | 0.136 | 0.189 | 3.065 | 4.598 | 5.939 | 3.054 | 4.588 | 5.956 |
| D. - MgCl ₂ | .205 | .236 | .266 | 3.042 | 4.078 | 4.632 | 3.014 | 4.027 | 4.748 |
| C. - MgCl ₂ | .285 | .307 | .333 | 3.054 | 4.033 | 4.295 | 2.998 | 3.899 | 4.460 |

TABLE VI A

Aspartic Acid (0.0100 molar)

| Salt | P_H | $\frac{b-a}{c}$ | b' | Estimated P_{G_1}' | α_2 | α_1 | P_{G_1}' | $\sqrt{\mu}$ |
|------------------------|-------|-----------------|--------|-------------------------|------------|------------|------------|--------------|
| C. - MgCl ₂ | 2.232 | -1.000 | -0.311 | 3.695 | 0.032 | 0.657 | 1.948 | 0.290 |
| D. - MgCl ₂ | 2.228 | -1.000 | -.321 | 3.750 | .028 | .651 | 1.958 | .218 |
| No salt | 2.228 | -1.000 | -.351 | 3.834 | .023 | .626 | 2.002 | .100 |
| D. - NaCl | 2.232 | -1.000 | -.327 | 3.752 | .028 | .645 | (2.072) | .218 |
| C. - NaCl | 2.232 | -1.000 | -.311 | 3.729 | .030 | .659 | 1.945 | .290 |
| C. - MgCl ₂ | 2.335 | -.800 | -.257 | 3.695 | .041 | .702 | 1.961 | .288 |
| D. - MgCl ₂ | 2.337 | -.800 | -.272 | 3.750 | .036 | .692 | 1.984 | .213 |
| No salt | 2.333 | -.800 | -.302 | 3.834 | .030 | .668 | 2.028 | .089 |
| D. - NaCl | 2.340 | -.800 | -.275 | 3.752 | .036 | .689 | 1.993 | .213 |
| C. - NaCl | 1.340 | -.800 | -.263 | 3.729 | .038 | .699 | 1.974 | .288 |
| C. - MgCl ₂ | 2.469 | -.600 | -.201 | 3.695 | .054 | .745 | 2.003 | .285 |
| D. - MgCl ₂ | 2.469 | -.600 | -.210 | 3.750 | .049 | .741 | 2.013 | .208 |
| No salt | 2.465 | -.600 | -.233 | 3.834 | .040 | .727 | 2.040 | .077 |
| D. - NaCl | 2.469 | -.600 | -.210 | 3.752 | .049 | .741 | 2.013 | .208 |
| C. - NaCl | 2.469 | -.600 | -.201 | 3.729 | .051 | .748 | 1.994 | .285 |
| C. - MgCl ₂ | 2.541 | -.500 | -.162 | 3.695 | .064 | .774 | 2.003 | .283 |
| D. - MgCl ₂ | 2.541 | -.500 | -.160 | 3.750 | .057 | .783 | 1.992 | .206 |
| No salt | 2.543 | -.500 | -.200 | 3.834 | .048 | .752 | 2.059 | .071 |
| D. - NaCl | 2.543 | -.500 | -.171 | 3.752 | .057 | .772 | 2.009 | .206 |
| C. - NaCl | 2.546 | -.500 | -.166 | 3.729 | .060 | .774 | 2.009 | .283 |
| C. - MgCl ₂ | 2.611 | -.400 | -.112 | 3.695 | .075 | .813 | 2.069 | .281 |
| D. - MgCl ₂ | 2.613 | -.400 | -.120 | 3.750 | .067 | .813 | 1.971 | .204 |
| No salt | 2.618 | -.400 | -.148 | 3.834 | .056 | .796 | 2.025 | .063 |
| D. - NaCl | 2.616 | -.400 | -.122 | 3.752 | .067 | .811 | (2.081) | .204 |
| C. - NaCl | 2.616 | -.400 | -.109 | 3.729 | .071 | .820 | 1.956 | .281 |
| C. - MgCl ₂ | 2.812 | -.200 | -.019 | 3.695 | .115 | .866 | 2.002 | .277 |
| D. - MgCl ₂ | 2.817 | -.200 | -.025 | 3.750 | .104 | .871 | 1.985 | .199 |
| No salt | 2.831 | -.200 | -.049 | 3.834 | .090 | .861 | 2.039 | .045 |
| D. - NaCl | 2.824 | -.200 | -.028 | 3.752 | .105 | .867 | 2.008 | .199 |
| C. - NaCl | 2.821 | -.200 | -.023 | 3.729 | .109 | .868 | 1.999 | .277 |
| C. - MgCl ₂ | 3.056 | 0 | .103 | 3.695 | .186 | .917 | 2.008 | .274 |
| D. - MgCl ₂ | 3.073 | 0 | .097 | 3.750 | .173 | .924 | 1.983 | .194 |
| No salt | 3.115 | 0 | .077 | 3.834 | .160 | .917 | 2.070 | .028 |
| D. - NaCl | 3.081 | 0 | .095 | 3.752 | .175 | .920 | 2.018 | .194 |
| C. - NaCl | 3.069 | 0 | .100 | 3.729 | .178 | .922 | 1.994 | .274 |
| C. - MgCl ₂ | 3.333 | 0.200 | .255 | 3.695 | .302 | .953 | 2.034 | .277 |
| D. - MgCl ₂ | 3.364 | .200 | .250 | 3.750 | .290 | .960 | 1.984 | .199 |
| No salt | 3.430 | .200 | .238 | 3.834 | .282 | .956 | 2.045 | .049 |
| D. - NaCl | 3.379 | .200 | .248 | 3.752 | .251 | .997 | (0.779) | .199 |
| C. - NaCl | 3.355 | .200 | .252 | 3.729 | .295 | .957 | 2.005 | .277 |

TABLE VI B
 Aspartic Acid (0.0100 molar)

| Salt | P_H | $\frac{b-a}{c}$ | b' | Estimated | | | P_{G_1}' | $\sqrt{\mu}$ |
|-----------------------|-------|-----------------|--------|------------|------------|------------|------------|--------------|
| | | | | P_{G_1}' | α_1 | α_2 | | |
| C. -MgCl ₂ | 2.812 | -0.200 | -0.019 | 2.03 | 0.857 | 0.124 | (3.657) | 0.277 |
| D. -MgCl ₂ | 2.817 | -.200 | -.025 | 2.04 | .856 | .119 | (3.682) | .199 |
| No salt | 2.831 | -.200 | -.049 | 2.05 | .857 | .094 | 3.812 | .045 |
| D. -NaCl | 2.824 | -.200 | -.028 | 2.04 | .858 | .114 | 3.711 | .199 |
| C. -NaCl | 2.821 | -.200 | -.023 | 2.03 | .861 | .116 | 3.701 | .277 |
| C. -MgCl ₂ | 3.056 | 0 | .103 | 2.03 | .913 | .190 | 3.684 | .274 |
| D. -MgCl ₂ | 3.073 | 0 | .097 | 2.04 | .915 | .182 | 3.726 | .194 |
| No salt | 3.115 | 0 | .077 | 2.05 | .921 | .156 | 3.846 | .028 |
| D. -NaCl | 3.081 | 0 | .095 | 2.04 | .916 | .179 | 3.740 | .194 |
| C. -NaCl | 3.069 | 0 | .100 | 2.03 | .916 | .184 | 3.714 | .274 |
| C. -MgCl ₂ | 3.333 | 0.200 | .255 | 2.03 | .953 | .302 | 3.694 | .277 |
| D. -MgCl ₂ | 3.364 | .200 | .250 | 2.04 | .955 | .295 | 3.739 | .199 |
| No salt | 3.430 | .200 | .238 | 2.05 | .960 | .278 | 3.843 | .049 |
| D. -NaCl | 3.379 | .200 | .248 | 2.04 | .956 | .292 | 3.760 | .199 |
| C. -NaCl | 3.355 | .200 | .252 | 2.03 | .955 | .297 | 3.725 | .277 |
| C. -MgCl ₂ | 3.626 | .400 | .428 | 2.03 | .976 | .452 | 3.709 | .281 |
| D. -MgCl ₂ | 3.672 | .400 | .424 | 2.04 | .977 | .447 | 3.765 | .204 |
| No salt | 3.746 | .400 | .419 | 2.05 | .980 | .439 | 3.851 | .065 |
| D. -NaCl | 3.677 | .400 | .424 | 2.04 | .978 | .446 | 3.771 | .204 |
| C. -NaCl | 3.660 | .400 | .426 | 2.03 | .978 | .448 | 3.749 | .281 |
| C. -MgCl ₂ | 3.937 | .600 | .614 | 2.03 | .988 | .626 | 3.711 | .290 |
| D. -MgCl ₂ | 3.981 | .600 | .612 | 2.04 | .989 | .623 | 3.760 | .218 |
| No salt | 4.032 | .600 | .610 | 2.05 | .990 | .620 | 3.817 | .100 |
| D. -NaCl | 3.979 | .600 | .612 | 2.04 | .989 | .623 | 3.758 | .218 |
| C. -NaCl | 3.957 | .600 | .613 | 2.03 | .988 | .625 | 3.733 | .290 |
| C. -MgCl ₂ | 4.347 | .800 | .805 | 2.03 | .995 | .810 | 3.714 | .290 |
| D. -MgCl ₂ | 4.394 | .800 | .805 | 2.04 | .995 | .810 | 3.762 | .218 |
| No salt | 4.465 | .800 | .804 | 2.05 | .996 | .808 | 3.835 | .100 |
| D. -NaCl | 4.401 | .800 | .805 | 2.04 | .995 | .810 | 3.769 | .218 |
| C. -NaCl | 4.384 | .800 | .805 | 2.03 | .995 | .810 | 3.751 | .290 |
| C. -MgCl ₂ | 6.0 | 1.000 | 1.000 | | | | | |
| D. -MgCl ₂ | 6.1 | 1.000 | 1.000 | | | | | |
| No salt | 6.5 | 1.000 | 1.000 | | | | | |
| D. -NaCl | 6.0 | 1.000 | 1.000 | | | | | |
| C. -NaCl | 6.3 | 1.000 | 1.000 | | | | | |

TABLE VI C

Aspartic Acid (0.0100 molar, 1 equivalent of base added to mother solution)

| Salt | P_H | $\frac{b-a}{c}$ | b' | P_G' | $\sqrt{\mu}$ |
|------------------------|--------|-----------------|-------|---------|--------------|
| No salt | 6.7 | 1.000 | 1.000 | | |
| C. - MgCl ₂ | 8.067 | 1.100 | 1.100 | 9.022 | 0.295 |
| D. - MgCl ₂ | 8.246 | 1.100 | 1.100 | 9.201 | .223 |
| No salt | 8.881 | 1.100 | 1.099 | 9.841 | .110 |
| D. - NaCl | 8.781 | 1.100 | 1.099 | 9.741 | .223 |
| C. - NaCl | 8.679 | 1.100 | 1.099 | 9.639 | .295 |
| C. - MgCl ₂ | 8.407 | 1.200 | 1.200 | 9.009 | .298 |
| D. - MgCl ₂ | 8.643 | 1.200 | 1.199 | 9.248 | .227 |
| No salt | 9.249 | 1.200 | 1.197 | 9.859 | .118 |
| D. - NaCl | 9.137 | 1.200 | 1.198 | 9.744 | .227 |
| C. - NaCl | 9.067 | 1.200 | 1.198 | 9.674 | .298 |
| C. - MgCl ₂ | 8.661 | 1.300 | 1.299 | 9.033 | .302 |
| D. - MgCl ₂ | 8.884 | 1.300 | 1.299 | 9.256 | .231 |
| No salt | 9.504 | 1.300 | 1.295 | 9.884 | .127 |
| D. - NaCl | 9.372 | 1.300 | 1.296 | 9.749 | .231 |
| C. - NaCl | 9.319 | 1.300 | 1.297 | 9.694 | .302 |
| C. - MgCl ₂ | 8.847 | 1.400 | 1.399 | 9.026 | .305 |
| D. - MgCl ₂ | 9.064 | 1.400 | 1.398 | 9.244 | .235 |
| No salt | 9.667 | 1.400 | 1.393 | 9.856 | .134 |
| D. - NaCl | 9.563 | 1.400 | 1.394 | 9.750 | .235 |
| C. - NaCl | 9.501 | 1.400 | 1.395 | 9.687 | .305 |
| C. - MgCl ₂ | 8.979 | 1.500 | 1.498 | (8.982) | .308 |
| D. - MgCl ₂ | 9.077 | 1.500 | 1.498 | (9.080) | .239 |
| No salt | 9.839 | 1.500 | 1.490 | 9.856 | .141 |
| D. - NaCl | 9.685 | 1.500 | 1.493 | 9.697 | .239 |
| C. - NaCl | 9.649 | 1.500 | 1.493 | 9.661 | .308 |
| No salt | 9.979 | 1.600 | 1.586 | 9.827 | .148 |
| D. - NaCl | 9.867 | 1.600 | 1.589 | 9.710 | .244 |
| C. - NaCl | 9.817 | 1.600 | 1.589 | 9.660 | .311 |
| No salt | 10.139 | 1.700 | 1.679 | 9.811 | .155 |
| D. - NaCl | 10.034 | 1.700 | 1.683 | 9.700 | .248 |
| C. - NaCl | 9.969 | 1.700 | 1.685 | 9.631 | .315 |
| No salt | 10.312 | 1.800 | 1.769 | 9.787 | .161 |
| D. - NaCl | 10.220 | 1.800 | 1.774 | 9.685 | .252 |
| C. - NaCl | 10.167 | 1.800 | 1.776 | 9.625 | .318 |
| No salt | 10.508 | 1.900 | 1.851 | 9.748 | .168 |
| D. - NaCl | 10.338 | 1.900 | 1.865 | (9.528) | .256 |
| C. - NaCl | 10.296 | 1.900 | 1.868 | (9.474) | .321 |
| No salt | 10.708 | 2.000 | 1.923 | (9.621) | .173 |

VI. Summary

When a divalent (or higher polyvalent) acid has titration constants (G') close together the titration indices (P_G') calculated by the method previously described are correct, only if the ionic strength is the same in all the experimental points.

With data at various ionic strengths we may first calculate approximate titration indices in this way, then plot them against $\sqrt{\mu}$, and draw a tentative curve for each index. At the $\sqrt{\mu}$ value of each experimental point we may obtain from these curves a series of more accurate titration indices. These may be used in calculating the final accurate titration indices, from which the dissociation indices may be obtained.

These dissociation indices (P_K') when plotted against $\sqrt{\mu}$ should give approximately straight line curves in dilute solution, the slopes of which indicate the agreement or disagreement with the modified Debye-Hückel equation given in the previous article.

The titration curve for citric acid (Fig. 1) demonstrates the magnitude of the effect of salts on a polyvalent acid.

15A-1907

THE RATE OF EVAPORATION OF MOLTEN CADMIUM IN A HIGH VACUUM*

BY ARTHUR A. SUNIER

In another research it was necessary to evaporate molten cadmium in a high vacuum. Some sixty separate evaporations were carried out, at different temperatures from 340°C to 425°C. Since the approximate average rate of evaporation was determined in each case, it has been thought advisable to publish these results, along with the theoretical rates of evaporation, and also a description of the apparatus employed.

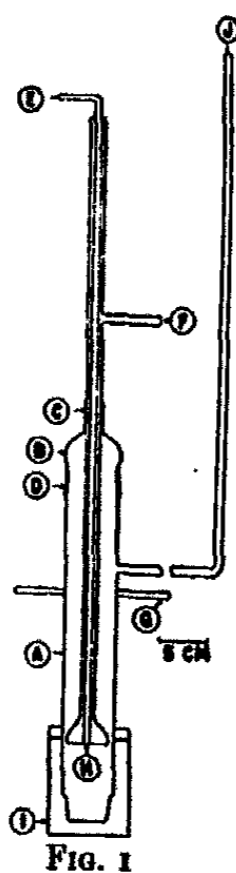
Apparatus

Two types of apparatus (shown in cross-section) were used. The first, shown in Fig. 1, was designed after many weeks experimentation on various types. A is the outer jacket, B a cap ground to fit A at the joint D. This ground joint must be made carefully in order that a high vacuum may be obtained in the apparatus. Connection was made at C between the cap B and the condenser H with deKhotinsky cement. This proved to be a very satisfactory joint. Cold water from the tap, is passed in at E and leaves the condenser at F. A metal bath I was employed in all the distillations. At first Newton's metal was used but it was soon discovered that the glass became quite dark after some fifteen distillations. Tin was used from then on without any such trouble arising. The joint D was protected from the heat of the bath by an asbestos shield G. Connection was made to the system at J. The connecting tube to J was made about 100 cm in length so the apparatus could be shaken. The whole apparatus was made of Pyrex.

The high vacuum was obtained with a Knipp, High-Speed, High-Vacuum Mercury Vapor Pump backed by a Cenco Hy-Vac oil pump. Pressures were measured with a McLeod gauge having a bulb of 544 c.c. capacity and capable of reading 5×10^{-6} mm with ease. This combination of pumps and gauge gave good results throughout the research. The gauge and mercury vapor pump as well as the whole system were made of Pyrex.

The apparatus shown in Fig. 2 was developed a little later than that shown in Fig. 1. It is more compact but has a still larger capacity. The stop-cock grease in the ground joint C never melted, since the cold water inside the condenser B kept the joint cool. No deKhotinsky joints appeared in this apparatus, which was also made of Pyrex.

* Contribution from the Chemical Laboratory of the University of Rochester. The material in this paper was reported in part at the Symposium on Physical Chemistry held in Rochester, New York, in January 1923.



Temperatures were obtained with a nitrogen-filled mercury thermometer placed in the metal bath. No attempt was made to correct the observed temperatures for length of exposed stem; nor was the thermometer calibrated carefully.

Procedure

The cadmium used in preliminary experiments came in the form of bars; the later material in rods. In each case pieces from 3 to 6 cm long were cut with the aid of a cold chisel. The charge varied with the various sizes of apparatus. Never more than 621 grams were placed in one apparatus. When the charge was in place heavy stop-cock grease was placed in the ground joint, the condenser filled with water, then put in place, and the apparatus sealed to the system. Pumps and heat (Bunsen burner) were generally started at the same time. When the metal in the bath was melted, the bath was raised to the position shown in the Figs. 1 and 2. More heat was applied until the temperature of the bath rose to 40 or 50 degrees above the melting point of cadmium. Since the apparatus was highly evacuated the heat was not conducted well to the material. This necessitated raising the temperature as just stated. As soon as it was known that the cadmium was melted (this was ascertained by lowering the bath for a moment and examining the

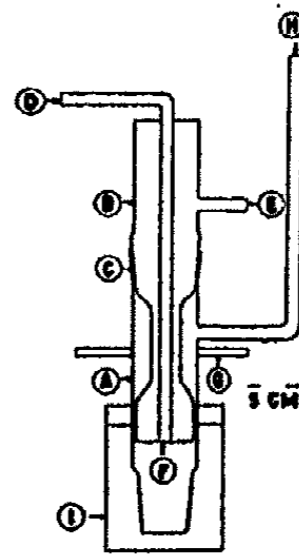


FIG. 2

TABLE I

Date: March 4, 1923
 Apparatus: No. 2, Distillation: No. 13
 Charge: 613 grams C. P. Cadmium

| Time | Temp. | Pressure | Remarks |
|-------|-------|--------------------------|------------------------|
| 12:40 | | | Pumps and heat started |
| 1:10 | 360° | 40 × 10 ⁻⁴ mm | Cd melted |
| 1:25 | 370° | 20 × 10 ⁻⁵ mm | Cd vaporizing |
| 1:35 | 378° | 16 × 10 ⁻⁵ mm | " " |
| 2:00 | 370° | 40 × 10 ⁻⁵ mm | " " |
| 2:30 | 368° | 50 × 10 ⁻⁵ mm | " " |
| 3:00 | 375° | 10 × 10 ⁻⁵ mm | " " |
| 4:00 | 380° | 5 × 10 ⁻⁵ mm | " " |
| 4:30 | 370° | 2 × 10 ⁻⁵ mm | " " |
| 5:00 | 375° | 2 × 10 ⁻⁵ mm | " " |

5:10 Distillation stopped
 Time: 4 hours
 Temperature: (average) 375° (rounded value)
 Yield: Condensate 270 g. Ll.
 Residue 343 g. Hl.
 Evaporation Rate: 270/(16)*(4) = 4.22 g. per sq. cm per hr.
 Theory: (375°) = 54 g. per sq. cm per hr.
 *For apparatus No. 2 the evaporating surface had an area of 16 sq. cm.

cadmium) the temperature was rapidly adjusted to the value desired. Accurate temperature control was not necessary hence regulating by hand was resorted to. A sample data sheet is given in Table I. Data sheets similar to that found in Table I were kept for all of the 60 distillations.

Results

The results of the sixty evaporations will be given in condensed form in Table II. The values in parentheses are the lowest and highest for any particular average temperature.

TABLE II
Experimental Rates of Evaporation

| Number of Runs | Average temp. °C | Average rate of evap. grams per sq. cm per hour |
|----------------|------------------|----------------------------------------------------|
| 1 | 335 | 2.0 |
| 5 | 345 | 4.4 (2.0-5.7) |
| 19 | 352 | 4.8 (2.1-10.0) |
| 12 | 363 | 5.1 (3.2-7.1) |
| 11 | 375 | 4.1 (2.4-9.2) |
| 5 | 381 | 4.5 (2.7-6.3) |
| 1 | 390 | 8.1 |
| 1 | 410 | 9.4 |
| 1 | 425 | 12.6 |

These results are plotted in Fig. 3; the dotted line represents the experimental rates of evaporation while the solid line represents the theoretical rates given in Table III.

The condensate always had a lustrous appearance and could rightly be described as beautiful. When two or three hundred grams of cadmium vaporized the condensate had very nearly a hemispherical shape. No difficulty whatsoever was encountered in removing the condensate from the glass condenser. A small amount (5-15 grams) of cadmium always condensed on the side of the condenser, but this was never far removed from the mass of material on the bottom of the condenser. Since the evaporating surface of the molten cadmium was always smaller than the condensing surface, very few atoms condensed on the outer walls of the apparatus.¹ Langmuir² and Wood³ have carried out experiments on the condensation of cadmium (and other) atoms on glass and metal surfaces. Langmuir's experimental results and his theory of condensation and reflection should be carefully studied by any interested in the subject of non-equilibrium evaporation.

¹ Egerton (Proc. Roy. Soc., 103A, 499 (1923)), working with zinc did not obtain this result, but his condensing surface was smaller than his evaporating surface; this accounts for the discrepancy.

² Proc. Nat. Acad. Sci., 3, 141 (1917).

³ Phil. Mag., (6), 32, 364 (1916).

In one particular distillation the condensate became so heavy that it broke away (partly) from the condenser, hence it was not cooled properly. The resulting condensate was composed of hundreds of little crystals easily visible with the naked eye. In this case it is almost certain that many atoms of cadmium re-evaporated. Volmer¹ and his associates have done some beautiful work on this phenomenon of crystal growth in a high vacuum. It is postulated that when atoms condense on a surface they are held temporarily in the force field of the surface, retaining, however, their motion until they either (1) evaporate or (2) are attracted to and held at the edges of the surface or (3) through contact with other atoms form the nucleus of another lattice layer. Whether (1), (2), or (3) will occur must depend on the vapor density and on the size of the surface. For further details the original should be consulted.

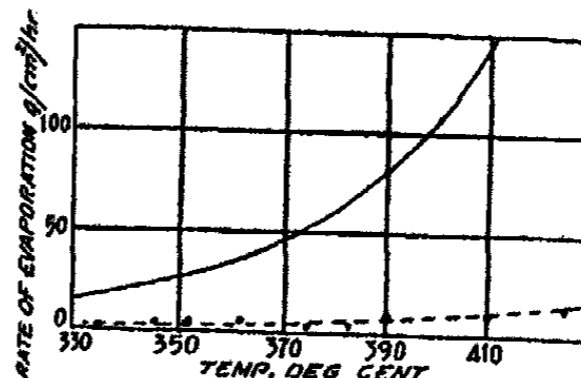


FIG. 3

Theoretical Rate of Evaporation

Herz² has, from kinetic theory considerations, deduced the following equation:

$$m = p \sqrt{\frac{M}{2\pi RT}}$$

where m is the number of grams evaporated from one sq. cm in one second, p is the vapor pressure in bars, M is the molecular weight of the substance, R is the gas constant (absolute units) and T is the absolute temperature.

For cadmium, the equation becomes $m = 22.26 \times 10^2 \times p \sqrt{\frac{1}{T}}$ g./cm²/hour when p is in mm.

Vapor pressure data have been calculated from the following equation:³

$$\log_{10} pcd = -\frac{5797.5}{T} - 1.203 \log_{10} T + 12.107$$

when p is in mm.

In Table III will be found the theoretical rates of evaporation using the vapor pressure data just mentioned, and the Herz equation.

TABLE III
Theoretical Rate of Evaporation of Cadmium

| Temperature (degrees C.) | Vapor pressure of cadmium in mm | Evaporation rate grams per sq. cm per hour |
|--------------------------|---------------------------------|--------------------------------------------|
| 330 | 0.141 | 12.8 |
| 350 | 0.276 | 24.6 |
| 370 | 0.517 | 45.3 |
| 390 | 0.933 | 80.6 |
| 410 | 1.623 | 138.4 |

¹Z. Physik, 5, 31, 188 (1921); 7, 1, 13 (1921); Z. physik. Chem., 102, 257 (1922).

²Ann. Physik, Chem., 18, 177 (1882). See also Langmuir: Phys. Rev., (2), 2, 329 (1913).

³"International Critical Tables", 3 (1928).

It must be emphasized that these theoretical rates of evaporation are for a perfectly clean evaporating surface, and for non-equilibrium conditions, that is, where *all* the atoms striking the condensing surface, condense.

Discussion of Results

All of the actual rates of evaporation have been compared with the theoretical rate, and the percentages calculated. In distillation No. 16 the rate of evaporation was only 4.2% of theory, while in distillation No. 48 it was 40.0% of theory; these are the minimum and maximum values. Five distillations yielded rates of evaporation from 0 to 5% of theory; twenty-three had rates from 6 to 10% of theory; eight had rates from 11 to 15% of theory; ten were in the group 16 to 20%, ten in the group 21 to 25%, one in the next group, none in the next and one in the last group (36 to 40% of theory). It is apparent that the distribution follows that of theory of probability as well as could be expected for a total of sixty experiments.

It so happened that it was highly desirable (in the research) to keep the rate of evaporation low, and yet have the temperature as high as possible. Several investigators¹ had shown (for mercury) that this could be accomplished by having the evaporating surface "dirty." In all of the distillations more or less oxide of cadmium was to be found on the surface of the molten cadmium. It seems almost certain that this is the reason for the low rates of evaporation obtained. At present there seems to be only one other possible reason and that is that only a fraction of the atoms that struck the cold condensing surface, actually condensed. Bennewitz² has investigated this problem when *solid* cadmium is evaporated in a high vacuum and the atoms strike a glass surface cooled with liquid air. For this case, Bennewitz shows that few if any atoms rebound. Evidence, presented above, seems to prove that little re-evaporation occurred. What little material that did not condense on the *bottom* of the condenser, usually formed in the early stages of the evaporation, that is before a layer of atoms of cadmium were formed on the bottom of the condenser. It is well known that condensation takes place more readily on the metallic surface, other factors remaining the same.

It would be interesting to determine the rate of evaporation when the evaporating surface was perfectly clean. Millikan³ has devised and described an apparatus which will allow fresh surfaces of the alkali metals to be produced in a high vacuum. It should not be particularly difficult to construct an apparatus which would allow of renewing the surface of molten cadmium during the course of an evaporation. Liquid air should be used as a cooling agent in the condenser. Unfortunately time did not permit experiments of this nature to be carried out and it seems improbable that the subject will be again taken up in the near future.

¹ Mulliken and Harkins: *J. Am. Chem. Soc.*, 44, 37 (1922); Knudsen: *Ann. Physik*, 47, 697 (1915).

² *Z. Physik*, 10, 169 (1922); *Ann. Physik*, (4) 59, 193 (1919).

³ *Phys. Rev.*, (2) 7, 362 (1916).

It is a pleasure to express my thanks to Professor W. D. Harkins, of the University of Chicago, for suggesting this problem and for his kindly interest and helpful suggestions throughout this research.

Summary

Apparatus is described which is suitable for the distillation of molten cadmium in a high vacuum; both condensate and residue may be removed with ease, at the end of the run.

Actual average rates of evaporation have been noted for about sixty runs; these rates are compared with the theoretical rates. The low results obtained are attributed mainly to one cause, a dirty evaporating surface.

THE REVERSAL OF TRAUBE'S RULE OF ADSORPTION

BY HARRY N. HOLMES AND J. B. MCKELVEY

The close connection between adsorption and surface-tension phenomena gives importance to Traube's rule. As originally announced by I. Traube¹

(and earlier touched upon by E. Duclaux²), "Such organic substances as alcohols, fatty acids, aldehydes, ketones, amines, and other organic non-electrolytes or weak electrolytes lower surface-tension to a greater degree as the length of the carbon chain increases in the homologous series."

H. Freundlich³ extends the rule to adsorption from aqueous solutions. "The adsorption of organic substances from aqueous solutions increases strongly and regularly as we ascend the homologous series."

Freundlich has pointed out repeatedly that while surface-tension lowering may be great in aqueous solution, it should be very much less in organic liquids which themselves have a very low surface-tension. Consequently adsorption should also be slight in amount. Yet Patrick and Jones⁴ observed notable adsorption from benzene, toluene, nitrobenzene and other organic liquids.

Since Freundlich's adsorption studies dealt with carbon, a non-polar solid, and water, a polar liquid, it occurred to us that the order of adsorption in a homologous series of fatty acids must be reversed when the acids are adsorbed on silica, a polar solid, from toluene, a non-polar liquid.

Obviously the highly polar $-\text{COOH}$ end of a fatty acid molecule must be oriented toward the silica surface and the non-polar alkyl group towards the toluene solvent.

Fatty acids of higher molecular weight are less polar and hence must be more strongly attracted by toluene and less strongly adsorbed on silica.

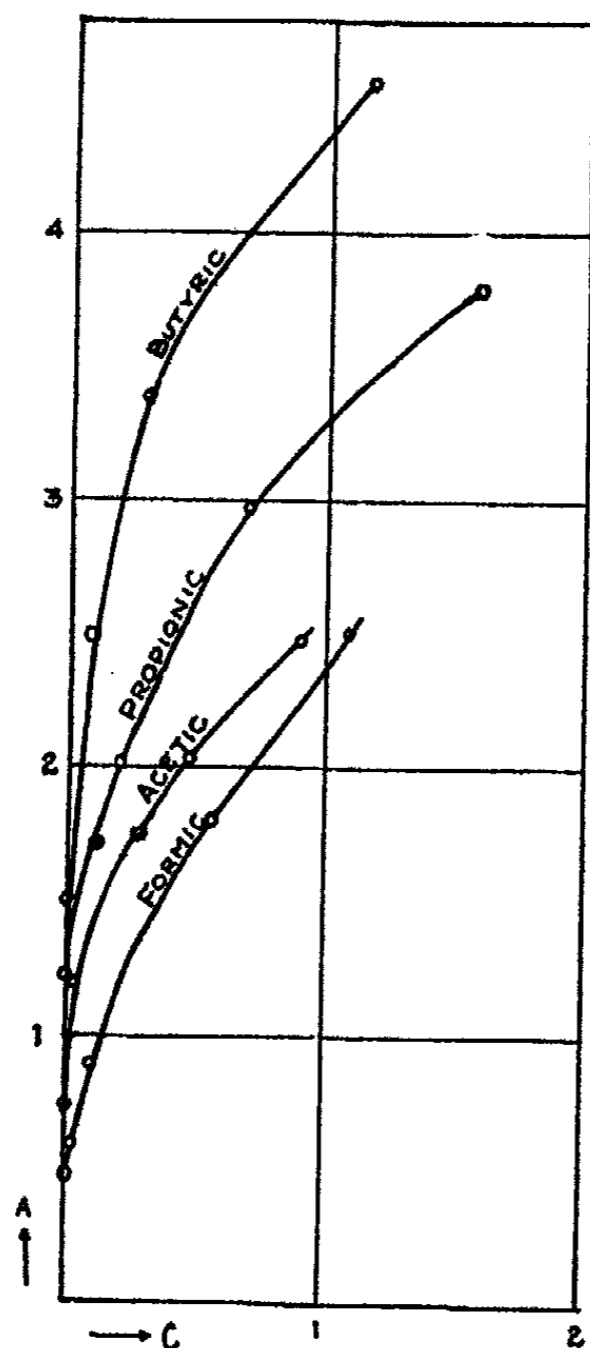


FIG. 1
Adsorption Isotherms of Aqueous Fatty Acid Solutions on Carbon. (Adapted by Freundlich from Traube's Surface-Tension Rule.)

¹ Ber., 17, 2294 (1884); J. prakt. Chem., (2) 34, 292, 515 (1886); Ann., 265, 27 (1891).

² Ann. Chim. Phys., (5) 13, 76 (1878).

³ "Colloid and Capillary Chemistry," 195 (1926).

⁴ J. Phys. Chem., 29, 1 (1925).

It may also be supposed that silica would be more readily wetted by the more polar lower members of the homologous series than by the higher members.

The toluene used was purified until it boiled at 110° - 111° , corresponding well with the standard 111° . The fatty acids were all of research quality, checked by titration against a pure base to values within 0.2% of theoretical acidity. These acids were all distilled from phosphorus pentoxide. The silica gel, prepared by Holmes¹ and his associates, was a white, chalky, porous powder passing through a 100-mesh sieve. It had been washed free

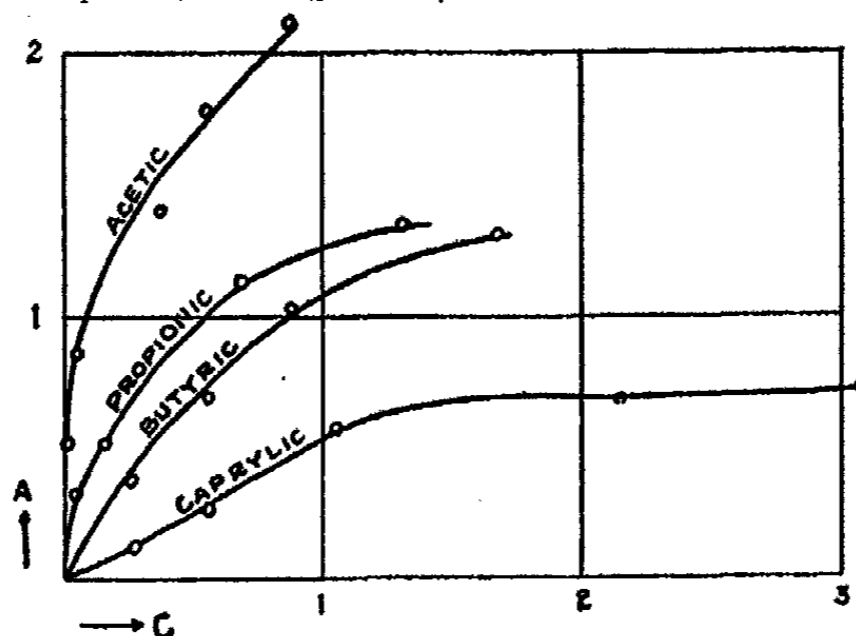


FIG. 2
Adsorption Isothermals of Solutions of Fatty Acids in Toluene on Silica Gel showing the Reversal of Traube's Rule.

from iron, sulfates, etc., by days of treatment with hot hydrochloric acid followed by hot water.

Titration of the fatty acids were made with $N/25$ and $N/75$ $\text{Ba}(\text{OH})_2$ using phenolphthalein as indicator. Caprylic acid was titrated in alcohol because of its very low solubility in water.

The adsorption was carried out in glass-stoppered flasks with 5 g. of silica gel and 50 cc. of solution in each case. The flasks were shaken 24 hours to insure equilibrium. After settling 10 cc. of the clear, supernatant liquid was removed and titrated with the base to determine the equilibrium concentration. From this and the original concentrations of fatty acid the specific adsorption was calculated.

On Fig. 2 the millimols of fatty acid adsorbed per gram of silica gel are plotted as A while the C represents the equilibrium concentration in grams. It is clearly seen that Traube's rule of adsorption, previously applied as in Fig. 1 to adsorption by carbon from water, is reversed when applied to adsorption by silica from toluene. Before publication we learned from F. E. Bartell of the University of Michigan that he had very recently discovered a similar reversal of Traube's rule when determining the adsorption of fatty acids from carbon tetrachloride by silica.

Oberlin College,
Oberlin, Ohio.

¹ Holmes, Sullivan and Metcalf: *Ind. Eng. Chem.*, 18, 386 (1926).

THE ADSORPTION OF GASES BY GRAPHITIC CARBON. II

X-ray Investigation of the Adsorbents

BY H. H. LOWRY AND R. M. BOZORTH

The data reported by Lowry and Morgan¹ on the adsorption of gases by graphitic carbon seem to disagree with the results obtained by Ruff and collaborators², which have led them to believe that graphite cannot be made to adsorb considerable quantities of gas, i.e., that carbon possesses a noteworthy adsorptive capacity only when in the "amorphous" form. In the original paper which contained the adsorption data it was pointed out that carbon prepared from graphitic acid had been shown by Burns and Hulett³ to have the same density as graphite and was accordingly classified by them as a finely divided graphite. That this conclusion was correct is indicated by a consideration of the X-ray evidence presented in this paper; for, in the X-ray photographs taken by us, diffraction bands are observed and show that the carbon prepared by the explosion of graphitic acid is graphitic in structure, and that the individual particles are flakes averaging approximately 50 atom diameters in breadth and 10 atom layers in thickness.

X-ray Measurements

For the X-ray measurements, samples of graphite I, II, and III, graphitic acid, and natural graphite were pressed into sticks sufficiently coherent to be handled without breaking. They were mounted in the X-ray beam, supported only at the ends so that no extraneous material, used to hold the samples in place, could have reflected X-rays onto the photographic film. The Mo K radiation from the X-ray target was filtered by zirconia so that only the α doublet was effective. The radial distance from the sample to the cylindrical film was 20.4 cm. The X-ray photographs were all taken in the same cassette to avoid errors due to centering.

The positions and approximate intensities of the lines on these photographs are shown in Fig. 1; they are in agreement with the structure of graphite as determined by Hassel and Mark⁴ and by Bernal⁵, and show that no appreciable orientation-effect was produced by pressing. Photographs of the three samples of carbon prepared from graphitic acid showed bands (a), (b) and (c) whose positions indicate that they correspond respectively to (002), (100)

¹ J. Phys. Chem., 29, 1105 (1925).

² Z. anorg. Chem., 148, 313; Z. angew. Chem., 38, 1164 (1925); Kolloid-Z., 38, 174 (1926). More recently in a paper appearing in Z. anorg. Chem., 167, 185 (1927) consideration is given to the data reported in our paper which was sent to Ruff in manuscript form Feb. 8, 1927.

³ J. Am. Chem. Soc., 45, 572 (1923).

⁴ O. Hassel and H. Mark: Z. Physik, 25, 317-37 (1924).

⁵ J. D. Bernal: Proc. Roy. Soc., 106A, 749-73 (1924).

and (110) ¹ reflections from natural graphite. The slight displacement of these bands from the normal (002) , (100) and (110) positions will be discussed later. The half-intensity widths of the bands on the photograph of graphite III are approximately 6 mm., 2.5 mm., and 3 mm., and are not very different for photographs of graphites I and II. Since the width of the lines on the photographs of natural graphite is about 1 mm., and the form and position of the samples and the width of the incident beam are the same in all cases, the broadening of the bands which can be ascribed to the structure of graphite III is about 5 mm. (0.02 radian) for (a) and 1.5 or 2 mm. (0.008 or 0.01 radian) for (b) and (c).

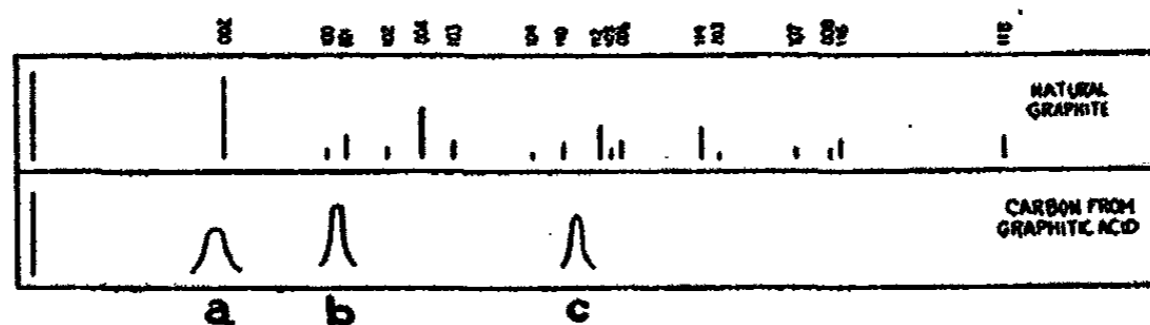


FIG. 1

Using Scherrer's² or Seljakow's³ formula for calculating crystal size from line width, the length of the crystal edge is found to be about 100 Å when bands (b) or (c) are considered, but only 30 Å or less when band (a) is considered. Since the inter-atomic spacings calculated from bands (b) and (c) correspond to the (100) and (110) spacings in graphite, and these planes are both perpendicular to the basal plane (001) corresponding to the band (a), we may conclude that the crystals are about 100 Å in breadth (measured in the basal plane perpendicular to the hexagonal axis) and about 30 Å in thickness (parallel to the axis). It is recognized that these dimensions refer to some average size of unit and that flakes are present which are both larger and smaller than the average.

For crystals of this shape, the planes most favorably situated for reflection are those perpendicular to the basal plane. Of these the greatest spacings are for (110) and (100) and only these are actually observed to reflect. Other planes, i.e., planes not containing the hexagonal axis, would be expected to reflect only under particularly favorable circumstances. Of such reflections that from (002) should be strongest, because it takes place at a small angle and its structure factor is a maximum,—this reflection is, in fact, by far the strongest from natural graphite. Since, on the photograph of graphite III, this reflection is faint, the absence of others needs no special explanation.

The displacements of the bands (a), (b) and (c) from the exact positions which would be expected for (002) , (100) and (110) lines, indicate that the basal planes are farther apart and the atoms in these planes closer together than in larger crystals of graphite. There is a similar difference in distances

¹ Hexagonal indices.

² P. Scherrer in R. Zsigmondy: "Kolloidchemie", 3 ed; pp. 394, 403-5 (1920).

³ N. Seljakow: Z. Physik, 31, 439-44 (1925).

between atoms in large graphite crystals as compared with diamond crystals. In diamond each carbon atom is surrounded tetrahedrally by four other carbon atoms 1.54 Å distant. In graphite, however, each carbon atom is surrounded by three atoms 1.45 Å distant in the same basal plane, but the distance to the nearest atom in the next basal plane is 3.39 Å; that is, a greater distance between atoms in one direction is accompanied by smaller distances between them in directions at right angles. No accurate quantitative measurements of the displacements of these bands were made, but it was estimated that the distance between atoms in the same basal planes is 1.42 Å and that between basal planes is 3.6 Å, as compared to the corresponding values 1.45 Å and 3.39 Å in large graphite crystals.

The X-ray data, then, are in accord with the idea that carbon from graphitic acid is made up of small graphite flakes, averaging about fifty atom diameters across and ten atom layers thick. Similar flakes of larger size are observed when graphite is treated with fuming nitric acid according to the method of Luzi.¹

A powder photograph of graphitic acid was also taken. This showed two bands having the same positions and approximately the same widths as (b) and (c) in Fig. 1, but no band (a). This suggests that in graphitic acid the carbon atoms in basal planes are arranged in the same way as they are in graphite, and the oxygen atoms place themselves between the planes, disturbing the regularity of their spacing.

The powder photograph of natural graphite showed one peculiarity which should be mentioned. The lines due to reflections from the basal planes, i.e., (002), (004) and (006) reflections, are especially sharp. The edges of the lines caused by the α_1 and by the α_2 Mo lines can be differentiated in these cases but not in others. This may be explained in two ways: (1) the crystal edge measured in the direction of the hexagonal axis is longer than that measured in other directions, (2)² the crystals are distorted in such a manner that the distance between basal planes is constant, but lateral displacement of these planes may occur with respect to each other. The first explanation seems improbable in view of the tendency of graphite to form thin flakes. The second explanation is a reasonable one, considering the short distance between neighboring atoms in each basal plane and the comparatively large distance between these planes. Such shearing of the crystal unit parallel to the basal planes, known to be planes of easy cleavage, would presumably require much smaller forces than would be required to compress or extend the crystal along the hexagonal axis. The weak bonding between basal planes thus has two opposite effects. It permits crystal distortion of a kind which broadens the reflections from planes inclined to the basal planes, leaving basal plane reflections relatively sharp. On the other hand it determines the shape of the fine crystals into which the larger crystals are mechanically or chemically broken, so that reflections from basal planes are broadened more than those from other planes. In large crystals, the first effect is the more important; in small crystals the second predominates.

¹ Luzi: Ber., 24, 4085 (1891).

² We are indebted to O. E. Buckley of these laboratories for this suggestion.

Discussion

Since the above data indicate that the carbon prepared from graphitic acid consists of small graphite crystals, we may conclude that graphite may be so prepared that it will have a considerable adsorptive capacity. A satisfactory explanation of the apparent contradiction to the data and conclusions of Ruff may be found in the fact that such graphites as have been studied in this investigation not only were very finely divided, but also, due to the breaking up of the crystal lattices during the preparation, must show considerable unsaturation. It is in this latter respect particularly that they differ from the mechanically subdivided graphite on which the adsorption measurements were made by Ruff and Hofmann¹; and it is believed that this difference accounts for the small adsorptive capacities observed by them with their samples of graphite. In other words, in order that a material have a considerable adsorptive capacity, it is necessary both that the extent of its surface be great and that the degree of unsaturation of the surface atoms be high. The first condition is favored by a decrease in particle size or increase in the volume of capillaries for a given weight of material, and the second, in addition, by the presence of crystal fragments and by a decrease in crystal size, so that the atoms which are less saturated by their neighbors, such as the corner atoms, form a greater percentage of the total.

The X-ray data of Debye and Scherrer² and Asahara³ have shown that the crystal structures of so-called amorphous carbons and graphite are essentially identical. In fact, Asahara has suggested that the word "amorphous", when applied to carbons, be replaced by the phrase "extremely minutely crystalline". Hofmann⁴, whose data on adsorption may appear to support the point of view expressed by Ruff, also questions the existence of any truly amorphous carbon on the basis of his own X-ray data. Since the "amorphous" carbons investigated have included adsorptive carbons and they have been shown to be graphitic, it would seem especially difficult to maintain the point of view that graphitic carbon cannot show any considerable adsorptive capacity. The data presented in this paper and in the original which contained the adsorption measurements indicate clearly that graphitic carbon can be made from graphite which shows an adsorptive capacity $1/3$ to $1/4$ that of the best adsorptive charcoal.

*Bell Telephone Laboratories,
New York City.*

¹ Ber., 59, 2433 (1926).

² Physik. Z., 18, 291 (1917).

³ Japan. J. Chem., 1, 35 (1922).

⁴ Ber., 59, 2443 (1926).

THE ENTROPY OF VAPORIZATION OF UNASSOCIATED LIQUIDS

BY JOHN CHIPMAN

Numerical relationships between the boiling point and heat of vaporization of unassociated liquids have proven useful in predicting heats of vaporization and vapor pressures as well as in distinguishing "normal" from associated liquids. Six empirical equations have been proposed expressing the heat of vaporization as a function of the boiling point only. These equations usually take their simplest form when expressed as entropy of vaporization. In this form they may be written as follows:

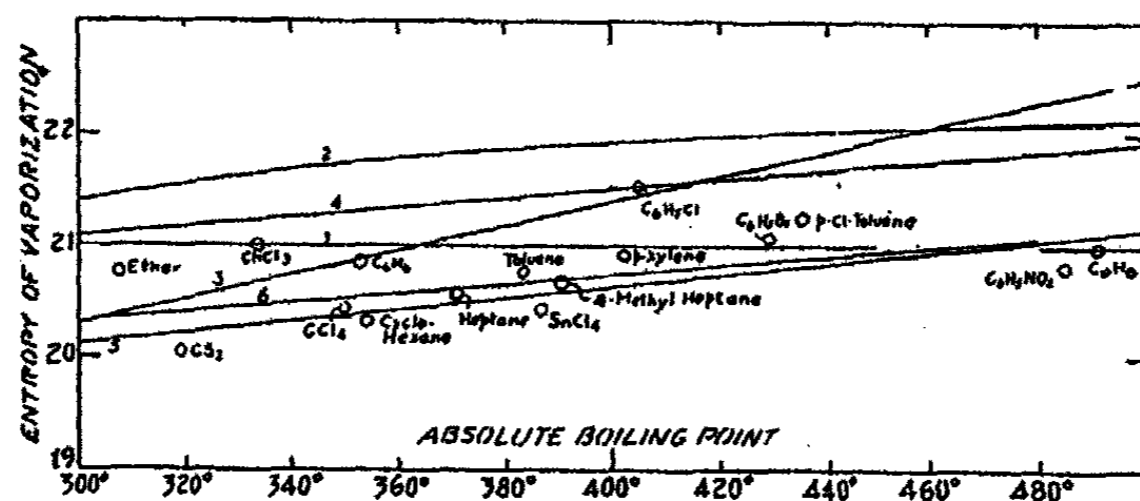


FIG. 1

$$\text{Trouton,}^1 \quad \Delta S = 21 \quad (1)$$

$$\text{Nernst,}^2 \quad \Delta S = 9.5 \log T_b - 0.007 T_b \quad (2)$$

$$\text{Bingham,}^3 \quad \Delta S = 17 + 0.011 T_b \quad (3)$$

$$\text{Forcrand,}^4 \quad \Delta S = 10.1 \log T_b - 1.5 - 0.009 T_b + 0.0000026 T_b^2 \quad (4)$$

$$\text{Kistiakowsky,}^5 \quad \Delta S = 4.578 \log (82.07 T_b) \quad (5)$$

$$\text{Mortimer,}^6 \quad \Delta S = 4.23 \left(-68/T_b + 4.877 + 0.0005 T_b \right) \quad (6)$$

Curves representing these equations in the temperature range 300° to 500°K are plotted in Fig. 1. The points, representing observed entropies of vaporization of unassociated liquids, are taken chiefly from measurements by Mathews;⁷ a few are quoted from Mortimer. It will be observed that any of the equations may be used in this range without serious error but that equations 1, 5 and 6 appear to fit more of the data than do the others. For a more complete test of the relative accuracy of the equations it is necessary to com-

¹ Trouton: Phil. Mag., (5) 18, 54 (1884).

² Nernst: Gött. Nachr., 1906.

³ Bingham: J. Am. Chem. Soc., 28, 723 (1906).

⁴ de Forcrand: Compt. rend., 156, 1493, 1648, 1809 (1913).

⁵ Kistiakowsky: J. Russ. Phys. Chem. Soc., 53, 256 (1921).

⁶ Mortimer: J. Am. Chem. Soc., 44, 1429 (1922).

⁷ Mathews: J. Am. Chem. Soc., 48, 562 (1926).

pare them at lower and at higher temperatures. This comparison is made in Figures 2 and 3. The points shown in these figures are taken from the following sources: oxygen and nitrogen, Dana;⁸ other low-boiling liquids, International Critical Tables;⁹ cadmium and zinc, calculated from free energy equations of Maier;¹⁰ lead, tin and gold, International Critical Tables;⁹ other high-boiling liquids, Jones, Langmuir and MacKay.¹¹

In the low-temperature range Equation 5 agrees with the observed values, except helium and hydrogen, with surprising accuracy; in the high temperature range it is the only one of the six that approaches the estimates of Jones, Langmuir and MacKay. For these reasons and because of its simplicity it is to be regarded as far superior to the other equations.¹²

Kistiakowsky's Equation

Kistiakowsky's derivation of Equation 5 is open to the criticism that it involves the cancellation of two quantities which are not apparently cancellable. The equation itself however contains no empirical constants other than the gas constant, R , and may be regarded as belonging to the class of semi-empirical equations which have been so useful in approximate calculations of entropy. In its simplest form the equation is written:

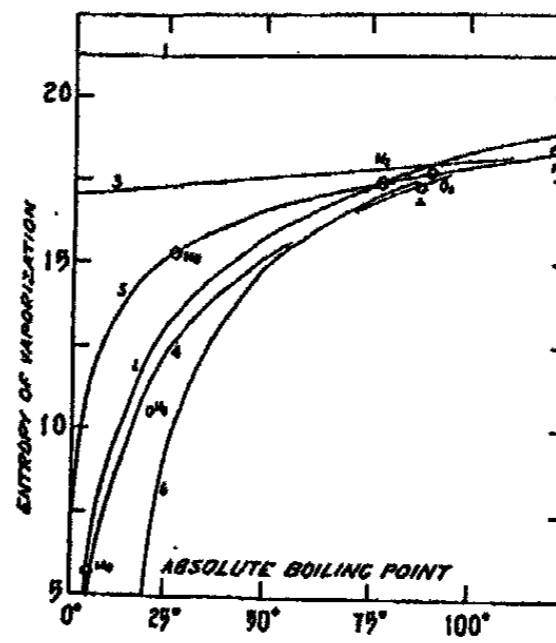


FIG. 2

$$\Delta S = R \ln V \quad (7)$$

where $\ln V$ is the natural logarithm of the molal volume of the vapor in equilibrium with the liquid (expressed in c.c.). R is of course expressed in the same units as ΔS . Assuming that the vapor is an ideal gas we may substitute RT for V at the boiling point (since $P = 1$); then:

$$\Delta S = R \ln RT_b \quad (8)$$

or
$$\Delta H = RT_b \ln RT_b \quad (9)$$

The second R must be expressed in c.c.-atmospheres and when this is done Equation 5 results.

Hildebrand's Rule

Hildebrand¹³ has shown that the entropy of vaporization for normal liquids is the same when evaporated to the same vapor concentration. Choosing arbitrarily temperatures at which the vapor concentration is 0.00507 mols

⁸ Dana: Proc. Am. Acad., 60, 241 (1925).

⁹ "International Critical Tables", 1, 102.

¹⁰ Maier: J. Am. Chem. Soc., 48, 356 (1926).

¹¹ Jones, Langmuir and MacKay: Phys. Rev., (2), 30, 201 (1927).

¹² Although Kistiakowsky's equation antedates that of Mortimer, the latter had no knowledge of it. Mortimer's equation fits the data from argon to copper fully as well as does Kistiakowsky's.

¹³ Hildebrand: J. Am. Chem. Soc., 37, 970 (1915).

per liter he found an average value of ΔS of about 27.4 calories per degree. Metals gave a somewhat lower value, about 26.3. Equation 7 is evidently another statement of this principle. According to this equation the entropy of vaporization to a concentration of 0.00507 mols per liter is 24.3 calories per degree. The discrepancy of two to three entropy units makes it seem worth while to recalculate some of Hildebrand's values on the basis of more accurate vapor pressure data than were available at the time of his publication.

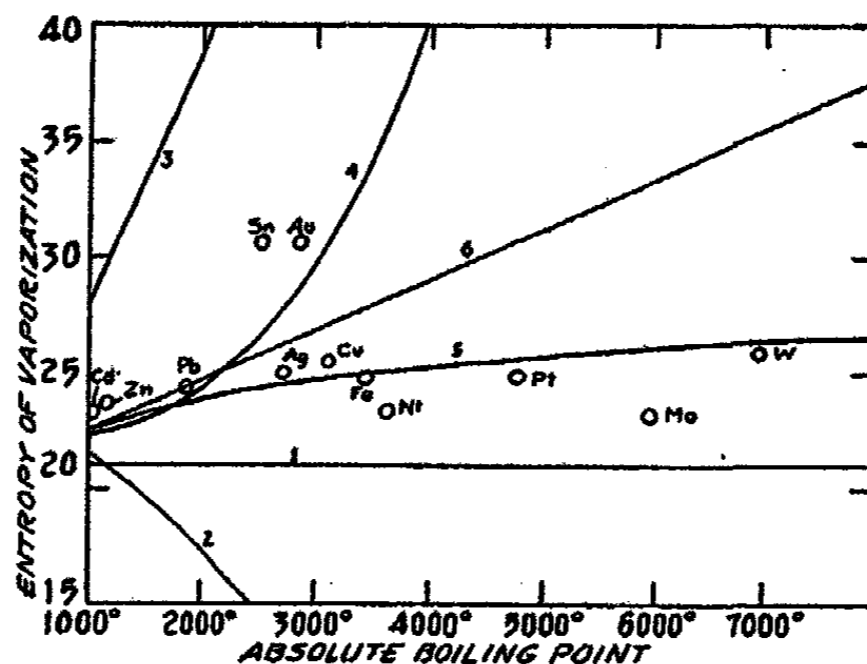


FIG. 3

Most investigators express the vapor pressure of a liquid by an equation of the form, $\log P_{\text{mm}} = A/T + B + CT$. If the vapor concentration is 0.00507 mols per liter, then by the gas law, $\log P_{\text{mm}} = -0.5 + \log T$. By combining these equations we may solve for the temperature T_1 at which the concentration of the vapor is 0.00507. The entropy of vaporization, ΔS_1 at this temperature is then obtained by differentiating the vapor pressure equation with respect to temperature and employing the Clausius-Clapeyron relationship. This is the analytical equivalent of the graphical method used

TABLE I
Entropy of Vaporization to a Concentration of 0.00507 Mols per Liter

| Substance | T_1 ,°K | ΔS_1 | Vapor pressure data |
|-------------|-----------|--------------|-----------------------------------|
| Nitrogen | 55.1 | 26.6 | Cath ¹⁴ (extrapolated) |
| Nitrogen | 55.1 | 26.8 | Henning ¹⁶ " |
| Oxygen | 65.8 | 27.2 | Cath ¹⁴ |
| Ethane | 143.5 | 26.9 | Loomis and Walters ¹⁶ |
| Naphthalene | 427. | 26.4 | Mortimer and Murphy ¹⁷ |
| Anthracene | 544. | 26.0 | Mortimer and Murphy |
| Cadmium | 962 | 25.2 | Maier ¹⁰ |
| Zinc | 1107 | 25.3 | Maier |

¹⁴ Cath: Proc. Acad. Sci. Amsterdam, 21, 656 (1919).

¹⁶ Henning: Z. Physik, 40, 775 (1927).

¹⁶ Loomis and Walters: J. Am. Chem. Soc., 48, 2051 (1926).

¹⁷ Mortimer and Murphy: Ind. Eng. Chem., 15, 1140 (1923).

by Hildebrand. The results of the calculations for several liquids are given in Table 1. The values are slightly lower than those obtained by Hildebrand but higher than the value predicted by Equation 7. Kistiakowsky's equation is therefore less reliable at lower temperatures than at the boiling point.

Entropy of a Monatomic Liquid

The entropy of a monatomic gas is given by the Sackur equation:¹⁸

$$S = R \ln (T^{3/2} w^{3/2} V) + C \quad (10)$$

By subtracting Equation 7 an expression is obtained for the entropy of a monatomic liquid:

$$S = 3/2 R \ln (Tw) + C \quad (11)$$

This equation holds fairly well for the liquefied rare gases (except helium) at their boiling points; for mercury however it is seriously in error. It may be considered at best a rough approximation to be used only in the neighborhood of the boiling point.

Summary

Equations expressing the entropy of vaporization of a normal liquid as a function of its boiling point have been compared graphically with recent experimental data. The equation of Kistiakowsky is found valid over a wide range of temperature.

This equation is in accord with Hildebrand's rule. Recent data lead to values for the entropy of vaporization to a concentration of 0.00507 mols per liter somewhat higher than that predicted by the Kistiakowsky equation.

An expression is obtained by which the entropy of a monatomic liquid in the neighborhood of its boiling point may be roughly estimated.

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¹⁸ See Lewis and Randall: "Thermodynamics", p. 455 (1923).

CATAPHORESIS AND THE ELECTRICAL NEUTRALIZATION OF COLLOIDAL MATERIAL

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1. Introduction

In a paper on the relation between the electrokinetic behavior and the exchange capacity of colloidal soil materials the author has established a quantitative relationship between the charge of the particles and certain properties of the soil material. This work emphasizes the importance of cataphoresis as applied to the study of electrical neutralization and to a determination of the isoelectric point.

While the electrical neutralization and mutual flocculation of oppositely charged colloidal dispersed material has been studied and much discussed in the literature, no attempts appear to have been made to study this behavior systematically in its application to problems of practical importance. Many such problems present themselves. The removal of colloidal suspended impurities is a matter of serious concern in many industries. The purification of water by the use of alum is an application of the above principle; but, here again, the different factors, qualitative and quantitative, which govern the electrical behavior of the suspended particles have not been investigated systematically. As a result of this the waterworks engineer often finds himself confronted with perplexing difficulties.

The use of alum and other electrolytes in the reclamation of alkaline soils suggests great possibilities, and research work in this direction should be accompanied by a study of the electrokinetic behavior of the different electrolyte-soil systems. The removal of colloidal material from raw sugar and molasses is another problem of economic importance which deserves a thorough investigation.

In many processes, such as the preparation of emulsions, sprays and precipitates to be used in pigments, etc., a high degree of dispersion is desirable and a study of the electrokinetic behavior of the dispersed material under different conditions would undoubtedly be of fundamental importance. Many other applications of cataphoresis could be suggested and it is safe to predict an important future for this method of dealing with colloidal behavior.

It is the object of this paper to give a detailed description of the cataphoresis cell used by the author and to give a few additional applications.

2. Cataphoresis

The electrical migration of suspended particles has in most cases been measured by observing the movement of the boundary between the suspension and the clear dispersing liquid when placed in a U-tube either of the type used by E. F. Burton,¹ or A. Coehn.²

¹ Phil. Mag., (6) 11, 44 (1906).

² Z. Elektrochemie, 15, 653 (1909).

This method is not accurate, however. In the first place the conductivity of the suspension is greater than that of the dispersing medium even if the latter consists of an ultrafiltrate of the former. The potential gradient is therefore not uniform. The movement of the particles at the boundary is proportional to the drop of potential at that point and this is constantly changing due to ionic migration. Then, since the current must flow for a considerable time to produce a measureable displacement, the effects of heating, electrolysis and polarization may be considerable; changes in concentration of the different ions must affect the charge of the particles. This probably accounts for the different rates with which the ascending and descending boundaries often move.

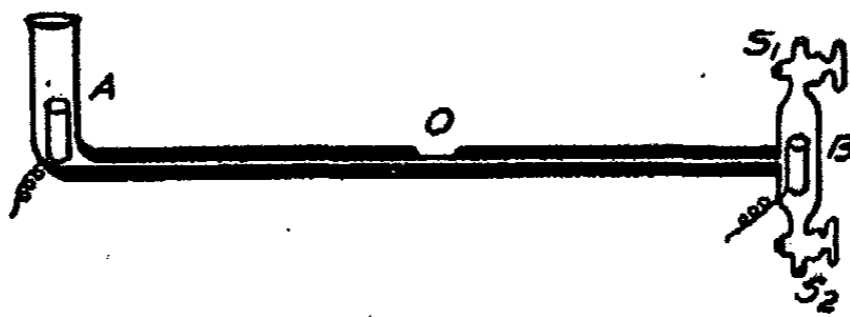


FIG. 1

The U-tube method is further limited to dispersed material and cannot be used after flocculation takes place, nor can the isoelectric point be determined.

Some of these difficulties have been overcome by the micro and ultramicroscopic methods of Cotton and Mouton,¹ The Svedberg,² R. Ellis,³ F. Powis,⁴ and others.

The most elaborate and accurate ultramicroscopic measurements have been made by The Svedberg and Hugo Anderson⁵ who have determined and pointed out the several errors connected with such measurements. They worked with a closed parallelepiped chamber and photographed the path of the particles in different depths of the chamber. From the velocities observed they calculated the electrosmotic movement of the liquid. Their results were in good agreement with theory. They obtained the best values when an alternating current was used. This method would probably be found too elaborate for most laboratory practice.

In a previous paper⁶ the author briefly described a simple cataphoresis cell with which about twenty measurements can be made in one hour with a fair degree of accuracy. Another but somewhat improved cell has later been constructed. Since this cell has never been fully described and in response to several requests, a detailed description is given below.

The cell is shown in Fig. 1 and consists of a thick-walled tube of 2.35 mm. inside diameter and 22.3 cm. long, terminating in two larger tubes as shown.

¹ "Les ultramicroscopes et les objets ultramicroscopiques" (1916).

² Nova Acta Soc. Sc. Upsaliensis, (4) 2, 149 (1907).

³ Z. physik. Chem., 78, 321 (1911).

⁴ Z. physik. Chem., 89, 91 (1914).

⁵ Kolloid-Z., 24, 156 (1919).

⁶ Mattson: Kolloidchem. Beihefte, 14, 227 (1922).

At O the tube is ground down to within 0.2 mm. of the inner wall. The plane surface is then polished or a piece of thin cover glass is pasted on the rough surface by means of Canada balsam. At right angles to O, on the side of the tube where the light is to enter, another plane surface is similarly made. This need not be made wider than the bore of the tube. Two large platinum electrodes are placed in the larger tubes A and B as near the entrance to the small tube as possible. The apparatus is sealed on a piece of wood and this is then firmly screwed onto the microscope platform. The cell is filled through tube A, which must be a little taller than B, the air escaping through stop-cock S₁. It is emptied through stop-cock S₂. Washing is accomplished rapidly in the same way. The particles are illuminated on the principle of

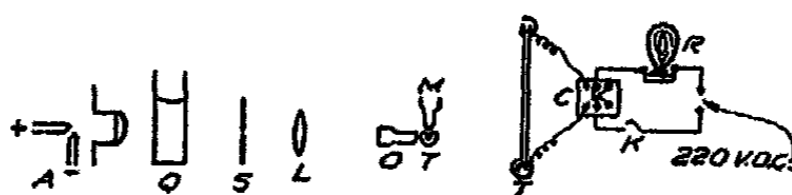


FIG. 2

the ultramicroscope, the source of light being an electric arc or a high-power incandescent lamp. The optical arrangement, which is similar to that of the ultramicroscope of Siedentopf and Zsigmondy, is shown in Fig. 2, where A is the arc lamp provided with a collecting lens, Q is a trough containing a saturated solution of alum to adsorb the heat, S is an adjustable slit, L is a lens with a focal length of 12 cm., O is a low-power objective (16 mm.) so placed that the image of the slit is focused inside the tube T directly under the microscope. T shows the tube in two positions. The electrodes are connected to a 220 volt direct current circuit. A 50-watt lamp is placed in series. By means of the commutator C the current is reversed¹.

The microscope used in this work was a Bausch and Lomb with an 8 mm. objective and eyepiece 7.5 giving a magnification of 150 diameters. The working distance of this objective (NA 0.50) is 1.6 mm. The eyepiece was provided with a scale which covered 0.4 mm. on the objective micrometer.

The P.D. at the electrodes deviated slightly from 205 volts. The potential gradient was therefore $205/22.3 = 9.2$ volts per cm. and the observed velocity V_1 of a particle expressed in $\mu/\text{sec.}$ in a gradient of one volt per cm. = $400/9.2 S$ where S is the time in seconds a particle requires to cover the scale.

The cataphoretic movement is measured in both directions, each observation covering on the average about 10 to 20 seconds, a stop-watch being used.

When the movement of the particles of an electronegative suspension is observed in a tube of the above description, it will be found that, observing successive layers from the top to the bottom of the tube, particles moving next to the wall move toward the cathode as if they carried a positive charge. This cathodic movement slows up further down, until a layer is reached where

¹ A cataphoresis cell of the above description is now supplied by Eimer and Amend, New York, and by the Arthur H. Thomas Company, Philadelphia.

the particles are apparently at rest. Below this layer the apparent movement is reversed, being now anodic as if the particles carried a negative charge, their speed increasing down to the center of the tube. The same changes in apparent movement repeat themselves from the center to the bottom of the tube.

The explanation is as follows: At the glass-water boundary is a double electrical layer, the water being positive and the glass surface negatively charged. The water will therefore be electrosmotically transported along the walls of the tube toward the cathode. Since now the tube is filled and the stop-cock closed, as much water as flows along the walls in one direction must return through the center in the opposite direction. In an annular layer somewhere between the axis and the wall the liquid must be at rest. The moving water carries the particles along and the observed velocity of the particles is $V_1 = v \pm V$ where v is the velocity of the particles relative to the liquid and V the velocity of the liquid. In the annular layer where $V = 0$, $V_1 = v$.

On the basis of some theoretical deductions of M. v. Smoluchowski¹ the following expression for the velocity of a liquid in the different parts of a closed capillary tube such as here described has been developed.

$$V = c \left(r^2 - \frac{1+z}{2} a^2 \right)$$

where r = distance from axis of tube,

a = radius,

c = a constant determined by the P.D. of the double layer,

z = a very small constant which, for so large tubes as here considered, can be put = 0.

From this expression it will be found that $V = 0$ when $r = 0.707a$.

The apparent speed of migration of the particles in a suspension of powdered quartz was measured in different parts of the tube. The second column in Table I gives the observed V_1 in $\mu/\text{sec.}$ 1 volt/cm. of the particles for different r values. The latter are expressed in terms of scale divisions on the microscope micrometer screw. The diameter of the tube was 524 divisions ($a = 262$).²

In a layer 185 ($= 0.707 \times 262$) scale divisions from the axis the particles moved with a speed of -2.9μ per sec. toward the anode. This is according to the formula the true speed of the particles since the liquid is at rest in this layer. Nearer the wall, at 217 scale divisions from the axis, the particles showed no apparent movement. Here the movement of the liquid must be equal and opposite to that of the particles or $+2.9 \mu/\text{sec.}$ By adding this value to the observed velocities of the particles V_1 we get V ; the velocity of the liquid at different depths of the tube as shown in the third column.

¹ Graetz: "Handbuch Elektr. Magn.", 7, 383 (1921).

² In measuring the diameter of the tube in microscope scale divisions it is necessary to use a low-power objective with a working distance equal at least to the depth of the tube. By allowing a sediment to settle on the bottom and a few gas bubbles to collect at the top of the tube these points are easily found.

TABLE I
Observed velocities of particles and calculated velocities of liquid in different depths of the tube

| r values | Velocity of particles V_1 observ. | Velocity of liquid $V = V_1 \pm 2.9$ | Velocity of liquid $V = c(r^2 - a^2/2)$ |
|----------|-------------------------------------|--------------------------------------|-----------------------------------------|
| 262 | +5.4 μ /sec. | +8.3 μ /sec. | +7.8 μ /sec. |
| 237 | +2.2 " | +5.1 " | +5.0 " |
| 217 | ± 0.0 " | +2.9 " | +2.9 " |
| 185 | -2.9 " | ± 0.0 " | ± 0.0 " |
| 162 | -4.3 " | -1.4 " | -1.8 " |
| 137 | -6.2 " | -3.3 " | -3.5 " |
| 112 | -7.9 " | -5.0 " | -4.9 " |
| 87 | -8.7 " | -5.8 " | -6.0 " |
| 62 | -9.7 " | -6.8 " | -6.8 " |
| 37 | -10.2 " | -7.3 " | -7.5 " |
| 0 | -10.2 " | -7.3 " | -7.8 " |

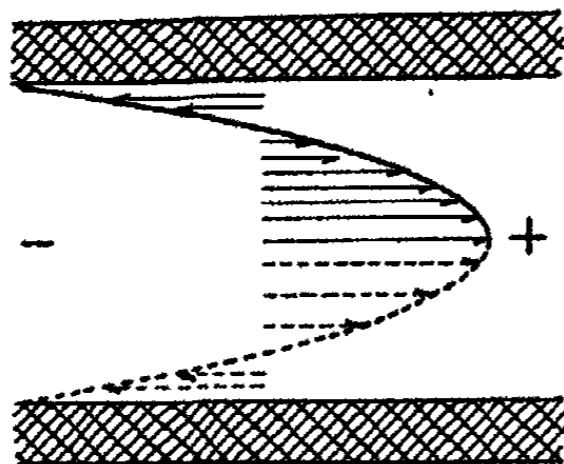


FIG. 3
Electroosmotic movement of water in a closed capillary tube.

We can also find V from the formula $V = c(r^2 - a^2/2)$, if we know the value of c . Putting the value of $V = +2.9 \mu$ at $r = 217$ we get $c = 0.000228$. Using this value for c we get the V values shown in column 4 which check fairly well with the V values of the third column.

These two series of V values representing the movement of the liquid in the different annular layers in the closed tube are expressed by the curve in Fig. 3. The arrows represent velocity vectors.

By keeping the microscope focused on a layer 0.7 of the radius from the axis of

the tube the true velocity of the particles is obtained directly. At this point the liquid must be at rest, independently of any change in the rate of electroosmosis, provided of course that the stop-cocks are kept well greased to prevent leaking. The cell must however always be kept absolutely clean. Certain electropositive materials such as acid proteins and basic dyes adhere tenaciously to the electronegative surface of the glass. The latter might thereby receive a different charge in different parts of the tube, causing an irregular electroosmotic flow of the liquid. The cell should be given a frequent cleaning with acid and alkaline solutions and should be left filled with a sulphuric acid bichromate mixture when not in use.

With the apparatus above described it is possible to measure the electrical migration not only of the individual particles but also that of the flocs after a suspension is flocculated and to study the effect of different electrolytes upon the charge and, what perhaps is the most important, the isoelectric

point of any system can be determined rapidly. The accuracy may be increased by taking the average of several measurements in each direction.

The particles under observation are 11 cm. away from either electrode and electrolysis cannot affect the charge of those particles since the current flows only a short time. The great distance between the electrodes allows the use of a high potential. This reduces the polarization potential to less than one percent of the electrode potential.

In the following tables the migration velocities of the particles are expressed in μ /sec. at a potential gradient of 1 volt/cm. From the migration velocity the electrokinetic potential ζ is calculated from the Helmholtz-Perrin formula:

$$v = \frac{\zeta H D}{4 \pi \eta}$$

where v = velocity of the particles,
 H = potential gradient in volt/cm.
 D = dielectric constant of the liquid,
 η = viscosity of liquid,
 hence the P. D. of the double layer:

$$\zeta = \frac{4 \pi \eta v}{H D}$$

The viscosity of water at the temperature of the laboratory is taken from the Smithsonian tables and the dielectric constant D is put equal to that of pure water at the same temperature.

When $v = 2.9$, $\mu = 2.9 \times 10^{-4}$ cm.

$$\zeta = \frac{4 \pi \times .01 \times .00029 \times 300 \times 300}{1 \times 80} = .041 \text{ volt}$$

300×300 is placed in the numerator to convert H and ζ into absolute units.

3. The Electrical Neutralization of Colloidal Clay by Aluminum Salts

In the following experiments the electrolyzed¹ supercentrifuge fraction of the Sharkey clay soil was used. 25 cc. of the clay suspension containing 10 mgms. of clay were rapidly mixed with 25 cc. of the salt solution and the mixture placed in test tubes provided with rubber stoppers. After 24 hours the degree of flocculation, which in the tables is represented with the letter x , was observed. One x signifies slight and four x 's complete flocculation. The tubes were then shaken and the cataphoresis measurements made.

Table II shows the gradual neutralization of the negative charge of the particles.

It will be seen that the lowest concentrations of AlCl_3 cause a proportionally much greater reduction of the charge than the higher concentrations, which only cause a very gradual further reduction of the negative charge until the mixture is isoelectric at a concentration of about 1.5 milliequivalents per liter. This is due to the fact that it is the products of hydrolysis

¹ Mattson: J. Agr. Res., 33, 553 (1926).

TABLE II
The electrical neutralization of electrodialyzed Sharkey clay by AlCl_3 ,
.200 gm. clay in one liter

| AlCl_3 milliequiv./liter | Flocculation after 24 hours | $\mu/\text{sec.}$ | P. D. millivolts |
|--------------------------------------|--------------------------------|-------------------|---------------------|
| 0 | 0 | -3.20 | -45.0 |
| 0.1 | XXX | -1.60 | -22.5 |
| 0.2 | XXXX | -0.80 | -11.3 |
| 0.4 | XXXX | -0.59 | -8.4 |
| 0.7 | XXXX | -0.45 | -6.3 |
| 1.0 | XXXX | -0.17 | -2.4 |
| 1.5 | XXXX | ± 0 | ± 0.0 |
| 2.0 | XXXX | +0.14 | +2.0 |
| 4.0 | XXXX | +0.49 | +7.0 |
| 8.0 | XXXX | +0.65 | +9.1 |

of the aluminum salt rather than the trivalent Al ion which reduce the charge most powerfully. Since the hydrolysis is proportionally greater in the more dilute solutions, the electrical neutralizing power is likewise proportionally greater.

That it is primarily the products of hydrolysis of the salts of aluminum and iron which are responsible for the electrical neutralization and flocculation of electronegative colloids has already been pointed out¹ but because of the importance of this fact for establishments where these substances are used for purification and clarification purposes the following experiment will be given here.

In a series of tubes the clay suspension was acidified and alkalinized with increasing quantities of HCl and NaOH respectively. AlCl_3 was then added at the rate of 1.5 milliequivalents per liter which, according to the previous experiment, was just sufficient to render the untreated suspension isoelectric. Table III gives the quantities of acid and alkali added, the rate of flocculation after mixing as well as the condition after 24 hours together with the charge on the particles or flocs in the different mixtures.

As will be noted the addition of the acid weakens the electrical neutralizing power of the AlCl_3 evidently as already pointed out by reversing the hydrolysis, while a partial alkalization causes activation. In the proportion of 1.5 milliequiv. AlCl_3 to 1.25 NaOH the particles attained their maximum electropositive charge moving at the rate of 3.1 μ per second toward the cathode. The pH at this point of highest activation was found in a number of cases to be about 5.2. A greater proportion of alkali reduces the positive charge, passes the isoelectric point and, with an excess of alkali, the system becomes strongly electronegative due to the adsorption of the OH ions.

It should be noted that the clay was electrodialyzed and therefore adsorptively unsaturated and strongly acid. Some of the base was therefore adsorbed by the clay. This accounts for the fact that the system was still

¹ Mattson: Kolloidchem. Beihefte, 14, 227 (1922).

TABLE III

The effect of HCl and NaOH upon the electrical neutralizing power of AlCl_3 in clay suspension. 1.5 milliequiv. AlCl_3 per liter was added to the acidified and alkalized suspensions

| Milliequiv. acid or base | Flocculation after mixing | 24 hrs. | $\mu/\text{sec.}$ 1 volt cm. | P. D. millivolts |
|-----------------------------|------------------------------|---------|---------------------------------|---------------------|
| 5.00 HCl | slow | XXXX | -0.48 | - 6.7 |
| 1.50 " | " | XXXX | -0.40 | - 5.6 |
| .50 " | " | XXXX | -0.21 | - 2.9 |
| — | rapid | XXXX | ± 0 | ± 0 |
| .10 NaOH | very rapid | XXXX | +0.37 | + 5.2 |
| .30 " | most rapid | XXXX | +0.98 | +13.8 |
| .50 " | slow | XXXX | +1.72 | +24.3 |
| .75 " | o | XXXX | +2.15 | +30.3 |
| 1.00 " | o | XXX | +2.60 | +36.3 |
| 1.25 " | o | XX | +3.10 | +43.7 |
| 1.40 " | o | XXXX | +2.20 | +31.0 |
| 1.50 " | rapid | XXXX | +0.43 | + 6.0 |
| 2.00 " | o | o | -3.20 | -45.0 |
| 4.00 " | o | o | -3.50 | -49.4 |

electropositive in the presence of equal proportions of AlCl_3 and NaOH. The proportion of AlCl_3 and NaOH which in the above case was found most efficient is of course of no importance since this proportion will vary with the reaction of the electronegative suspension.

In his earlier work referred to above the author found that CuSO_4 behaves in the same way as the salts of iron and aluminum. Without alkali the CuSO_4 caused only the usual reduction of the charge on quartz particles produced by other divalent cations. If the sulphate was partly alkalized it charged the particles positively, while an excess of alkali gave rise to a second reversal in the sign of charge.

The above results are represented graphically in Fig. 4. The sharp bend in the lower part of the curve shows a very narrow limit of maximum activity. This limit corresponds to the formation of the maximum quantity of the electropositive colloidal oxychloride. On the more acid side the normal AlCl_3 predominates, and while the Al ions suppress the negative charge considerably they do not entirely neutralize it. On the alkaline side the normal $\text{Al}(\text{OH})_3$ is formed and this material is, in the slightest excess of alkali, itself electronegative. Alumina is an electrical ampholyte and its maximum activity as a positive sol appears to coincide with a pH of about 5.2.

In order to determine the electrical neutralizing power of alkalized AlCl_3 in the proportion of 1.25 milliequivalents of NaOH to 1.5 of AlCl_3 experiments were carried out with the same clay suspension by adding increasing quantities of the two electrolytes in this proportion; it was found that slightly more than 0.5 milliequivalents of the alkalized AlCl_3 was sufficient to render 0.2 gm. of the clay material isoelectric as compared to 1.5

milliequivalents of normal AlCl_3 . This is equivalent to .0085 gm. Al_2O_3 in the former and .0255 gm. Al_2O_3 in the latter case. The isoelectric ratio of Al_2O_3 to clay is therefore under the most favorable condition $.0085/.2 = .043$ which means that 43 mgms. of Al_2O_3 are sufficient for the electrical neutralization of one gram of the clay here used. It should be added that different clays differ very much in this respect. The red and yellow varieties which have a high sesquioxide content are only weakly electronegative and are easily neutralized, while clays with a high silica content are strongly electronegative and show a high isoelectric ratio.¹

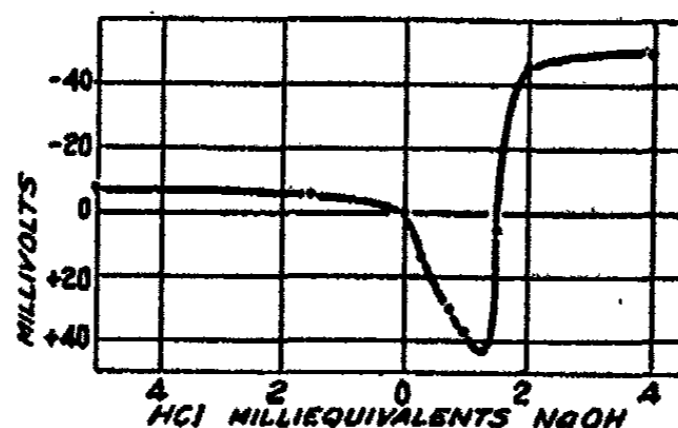


FIG. 4
Displacement of the electrokinetic potential by HCl and NaOH in an isoelectric mixture of 1.5 milliequivalents AlCl_3 and 0.2 gram clay per liter (comp. Table III.).

From the above experiments it follows that, where an aluminum salt is to be used as a flocculating agent of electronegative material, the highest efficiency can only be attained by adjusting the pH to a point at which the products of hydrolysis of the aluminum salt constitute an electropositive sol of maximum activity. For the chloride of aluminum this pH is about 5.2. Whether acid or alkali is to be added to the suspension depends of course upon the reaction of the latter. It is evident that the addition of a salt of aluminum to an alkaline water would at first result in the formation of electronegative $\text{Al}(\text{OH})_3$, which would have no effect upon the stability of the electronegative material in suspension. A great saving of alumina would be effected by the addition of a certain quantity of acid and by a determination of the isoelectric ratio.

In view of the proposed treatment of alkaline soils with salts of aluminum the importance of investigations along the above lines will be realized. If insufficient amounts of the salt were applied, the normal $\text{Al}(\text{OH})_3$ would be formed which, in excess of alkali, is itself electronegative and would therefore be without effect. An excess of salt might be injurious to plants and would not improve the soil structure as much as the optimum amount, which could be determined by the above method of electrical neutralization.

It should be added that the floc produced by the partly alkalized AlCl_3 was found to be much more stable than that formed by AlCl_3 alone or with HCl. A few decantations caused dispersion of the floc produced by the last

¹ Mattson: J. Am. Soc. Agron., 18, 458 (1926).

two methods while the first-mentioned floc remained stable after a great number of washings.

A significant fact is that the greatest activity of the aluminum compound as an electrical neutralizing agent lies in a region of great insolubility. Very little aluminum is therefore left in the solution if flocculation takes place at the isoelectric point.

Experiments with alum showed that while the flocculating power of this salt is equal to that of the chloride,¹ its neutralizing effect on the negative charge of the clay particles is weaker. A concentration of alum of 1.5 milliequivalents per liter with respect to the Al ion reduced the electrokinetic potential of the clay particles from -45.0 to -2.4 millivolts (comp. Table III). Even a concentration of 8.0 milliequivalents per liter left the particles

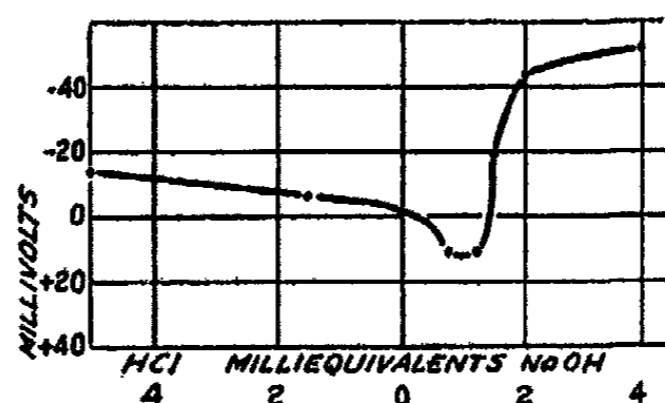


FIG. 5
Displacement of the electrokinetic potential by HCl and NaOH in a mixture of 1.5 milliequivalents alum ($\frac{K_2Al_2(SO_4)_4}{6}$) and 0.2 gm. clay per liter.

slightly electronegative. A partial alkalization activated the alum but to a lesser degree than in the case of $AlCl_3$. Hydrochloric acid and sodium hydroxide were added to the clay suspension in a series of tubes as in the experiment with $AlCl_3$ and for comparison 1.5 milliequivalents per liter of recrystallized alum were added. Fig. 5 shows the displacement of the electrokinetic potential caused by the acid and alkali. The difference in behavior of the two salts of aluminum is due to the sulphate ions which are present in excess in the alum solution. It will be shown later that the anions, especially the divalent and polyvalent, cause a displacement of the charge of colloidal particles in the electronegative direction. The addition of K_2SO_4 to the $AlCl_3$ -clay mixture showed a similar displacement.

4. Influence of Anions and Cations on the Electrokinetic Potential and the Electrical Neutralizing Power of Clay Particles

In a previous paper² the author has shown that the quantities of methylene blue required to render a given quantity of clay isoelectric is directly proportional to the base exchange capacity of the clay material at the same pH. This was explained on the assumption that the methylene blue cation displaces the common cations forming a nondissociated adsorption compound with the clay complex. In the presence of other electrolytes the quantity

¹ Flocculation takes place over a wide range on either side of the isoelectric point.

² Mattson: J. Am. Soc. Agron., 18, 458 (1926).

of the dye required to neutralize the negative charge on the clay particles may be greatly affected, the effect being in general such that the more active anions increase the isoelectric ratio of methylene blue to clay while the active cations decrease this ratio. This is illustrated in Fig. 6, where the abscissas represent the quantities of methylene blue added to the suspensions and the ordinates the corresponding velocities of electrical migration in $\mu/\text{sec.}$ for 1 volt/cm.

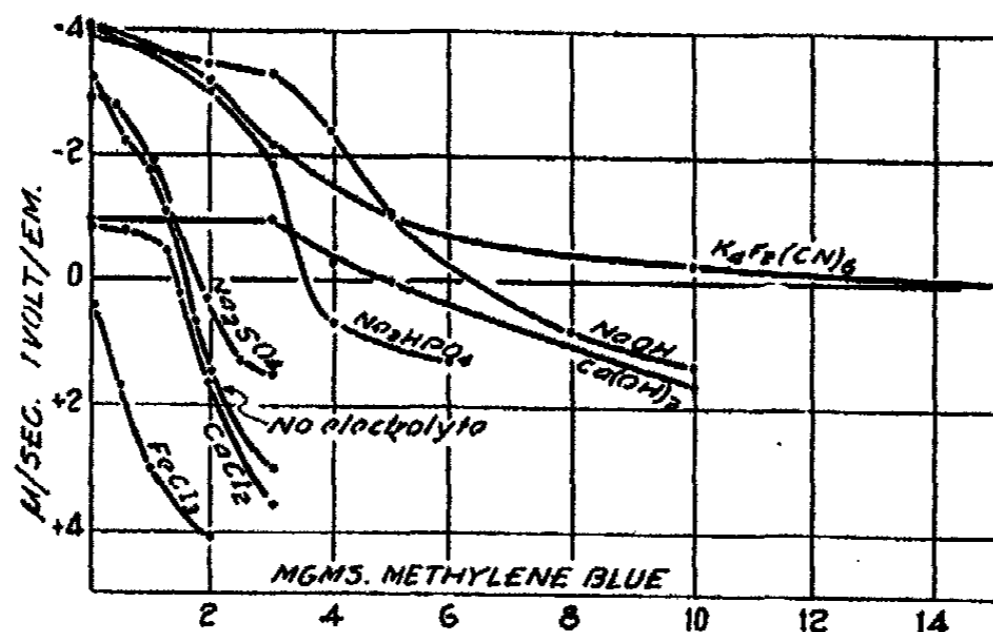


FIG. 6
Influence of anions and cations on the electrokinetic potential and the electrical neutralizing power of clay particles.

The results were obtained by mixing 25 cc. of the suspension containing 10 milligrams of clay to which the electrolytes had been added with 25 cc. of the methylene blue solution and after 24 hours measuring the cataphoretic movement. The concentration of the electrolytes was in each case 1.5 milliequivalents per liter.

It will be seen that anions, especially those with a high valence together with the OH ions, cause a displacement of the isoelectric point in the direction of greater methylene blue concentrations, while the di- and trivalent cations cause an opposite displacement. While the more active anions effect a greater steepness of the curves in the electronegative region and a flattening of the curves in the electropositive region, the active cations produce an opposite effect. Where both of the ions are active as in $\text{Ca}(\text{OH})_2$ the curve becomes flatter in both regions.

It will also be noted that the electrical neutralizing power of the clay is independent of the initial charge of the particles. The addition of $\text{Ca}(\text{OH})_2$ reduced the migration velocity from 3.2 to 1.0 $\mu/\text{sec.}$ while the quantity of methylene blue required to neutralize the negative charge of the particles increased from about 1.6 to 5.0 milligrams. The hydroxide, phosphate, and ferrocyanide of sodium all increase the migration velocity to about 4 $\mu/\text{sec.}$ but the electrical neutralizing power of the clay has become proportionally much greater.

These facts lead to the recognition of two factors of electrokinetic energy similar to all other forms of energy: an intensity factor and a quantity factor. The former is represented by the electrokinetic potential and the latter expresses itself in the form of the electrical neutralizing power and represents the total quantity of adsorbed ions. The electrokinetic potential is due to the existence of an electrical double layer resulting from an unequal adsorption of ions of opposite sign of charge. But it appears improbable that all of the adsorbed ions exist in the form of a double layer. Calculations made by the author¹ indicate that only a small fraction of the ions adsorbed by soil materials exist in this condition. If this were not so it would be difficult to explain the above observations. The adsorption of one ion in excess of the other of a pair of ions must be limited by electrostatic attraction. The value of this limit will depend upon the nature of the ions, size and hydration probably being the most important factors as already pointed out by Wiegner.² From the above experiment it is evident that the association tendency of the Ca ions is greater than that of the more highly hydrated Na ions or, what amounts to the same thing, the dissociation tendency of the Na ions is the greater.

The fact that much more methylene blue was required to neutralize the negative charge of the clay after $\text{Ca}(\text{OH})_2$ had been added, although this addition resulted in a reduction of the initial charge, is to be explained as follows: The methylene blue cations which are strongly adsorbed neutralize the free charges of adsorbed anions. The Ca ions in the outer layer are thereby released and diffuse into the solution where they are electrically balanced by the anions of the dye. As the electrokinetic potential is reduced the Ca ions in the inner layer are set free and this displacement continues until all the negative charges due to adsorbed anions have been neutralized by the methylene blue cations, when the material is isoelectric.

We find a perfect analogy in the pH and titration value of an acid solution. Just as an acid may have a low hydrogen ion concentration but a high titration value, or vice-versa, colloidal particles may have a weak charge but a high electrical neutralizing power or vice versa. The two processes differ however inasmuch as the titration value of an acid is a fixed quantity while the electrical neutralization of colloidal materials, which depends upon ionic equilibria, varies with the nature and concentration of the ions.

In flocculating a suspension of denatured albumen with Na-acetate-acetic acid mixtures L. Michaelis and P. Rona³ found that, for flocculation the most active hydrogen ion concentration was displaced toward the acid side by the active anions while cations caused a displacement toward the alkaline side. This displacement of the pH at which flocculation took place is in reality a displacement of the isoelectric point. The acid side in their experiment corresponds to the positive side in the above experiments. The methyl-

¹ Mattson: J. Agr. Res., 33, 553 (1926).

² Kolloid-Z., 36 (Zsigmondy Festschrift) 341 (1925).

³ Biochem. Z., 94, 225 (1919).

one blue in the above case plays the same part as the H ions in the case of albumen which is an ampholyte. We see therefore the same principle disclosed in both cases.

5. The Electrical Behavior of the Colloidal Material in Milk, Raw Sugar and Molasses

The proteins in milk consist chiefly of casein and albumen. These are true ampholytes and like gelatin are isoelectric at a hydrogen ion concentration of 2×10^{-8} or a pH of 4.7 as determined by L. Michaelis.¹ The pH of fresh milk is usually 6.6 and the electrical migration of the proteins is anodic. The proteins exist in the form of proteinates and their ions as anions, hence the electronegative behavior. On the acid side of the isoelectric point the proteins combine with acids and become cathodic.

When milk sours, or when an acid is added, the caseinates and albuminates are decomposed and the anodic movements become slower until at a pH of 4.7 there is no migration. A further increase in the hydrogen ion concentration results in a reversal in the direction of migration. The proteins have become electropositive.

Table IV shows the effect of HCl upon the electrical behavior of the milk proteins.

TABLE IV
Effect of HCl upon the electrical migration of milk proteins.
0.2 cc. fresh pasteurized milk diluted to 20 cc.

| HCl cc. 0.01 N in 20 cc. | Flocculation | μ /sec. within 1/2 hour | P. D. milli- volts | pH |
|--------------------------------|--------------|-----------------------------------|--------------------------|-----|
| 0 | o | -2.92 | -41.2 | 6.7 |
| 0.5 | o | -2.24 | -31.6 | 5.7 |
| 1.0 | o | -1.41 | -19.8 | 4.9 |
| 1.2 | XXXX | ± 0 | ± 0 | 4.7 |
| 1.4 | o | +1.26 | +17.7 | 4.6 |
| 1.6 | o | +1.72 | +24.3 | 4.5 |
| 1.8 | o | +2.30 | +32.4 | — |
| 2.0 | o | +2.47 | +34.8 | — |

The initial migration velocity was -2.92μ /sec. The calculated P.D. was -41.2 which agrees well with the values observed by J. Loeb² in a solution of Na-gelatin at the same pH.

At a concentration of 1.2 cc. N/100 HCl in 20 cc. of the diluted milk the proteins were isoelectric and coagulated completely.

The action of the HCl is, according to the now generally accepted view, purely chemical in nature, the proteins being true ampholytes. The action of a basic dye like methylene blue upon the milk proteins is different, and probably best accounted for by assuming an adsorption and electrical neu-

¹ "Die Wasserstoffionkonzentrationen", 54 (1914).

² "Proteins and the Theory of Colloidal Behavior", 138 (1922).

tralization of oppositely charged bodies, the negative proteins and the positive ions of the dye.

Table V shows the effect of methylene blue on the electrical behavior of milk proteins.

It required about 4.1 mgm. of the dye to produce electrical neutralization of 0.2 cc. fresh milk when diluted to 20 cc. with freshly distilled water. Coagulation, it will be seen, extends slightly on either side of the isoelectric point.

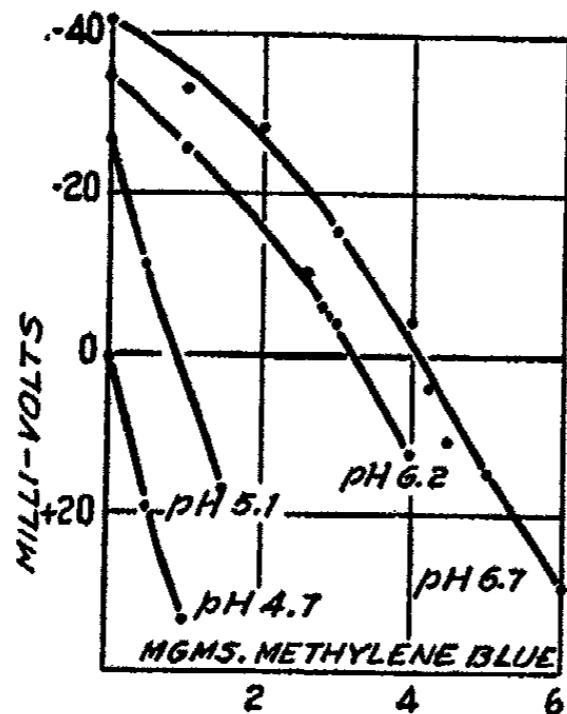


FIG. 7
Electrical neutralization of milk proteins at varying pH values by methylene blue.

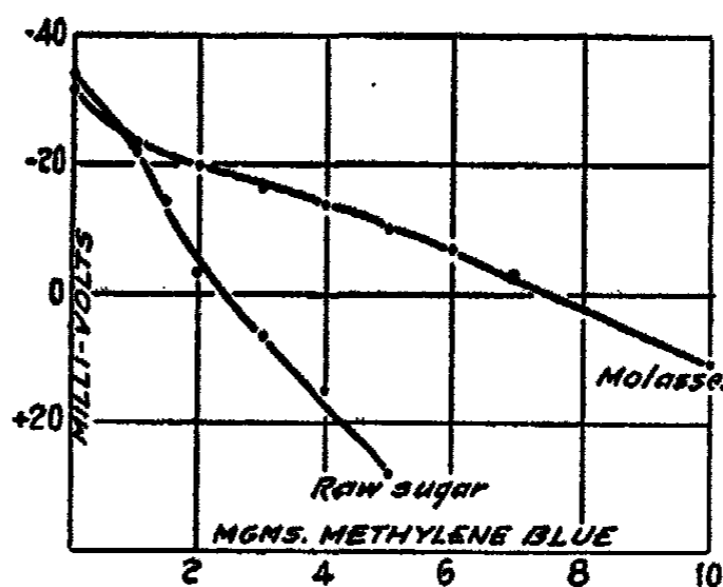


FIG. 8
Electrical neutralization of colloidal material in raw sugar and molasses by methylene blue.

TABLE V
Electrical neutralization of milk proteins by methylene blue.
0.2 cc. fresh pasteurized milk diluted to 20 cc.

| Methylene blue mgms. | Flocculation | $\mu/\text{sec.}$ within $\frac{1}{2}$ hour | P. D. |
|----------------------|--------------|------------------------------------------------|-------|
| 0 | o | -2.92 | -41.2 |
| 1.0 | o | -2.30 | -32.4 |
| 2.0 | o | -2.00 | -28.2 |
| 3.0 | x | -1.05 | -14.8 |
| 4.0 | XXXX | -0.24 | -3.4 |
| 4.2 | XXXX | +0.33 | +4.6 |
| 4.5 | XXX | +0.78 | +11.0 |
| 5.0 | x | +1.08 | +15.2 |
| 6.0 | o | +2.11 | +29.8 |

Since souring renders the milk less electronegative, the same sample of milk was placed in the cooler and at 48 hour intervals the experiment with methylene blue was repeated. After two days the pH of the diluted milk was 6.2, after four days it was 5.1, and after six days it was 4.7, and the

coagulum was isoelectric. The results of these and the above experiment with methylene blue are shown in Fig. 7 in which the abscissas give the concentration of the dye and the ordinates the calculated P. D.'s.

It will be seen that, as the acidity of the milk increases, less of the methylene blue is required to reach the isoelectric point. It thus appears that the freshness of milk may be determined by its electrical neutralizing power.

Fig. 8 shows the electrical behavior of the colloidal material in raw cane sugar and in molasses from beets. Each tube contained 100 mgms. of the sugar or molasses in 50 cc. water. The abscissas show the number of mgms. methylene blue added to each tube.

It will be seen that the colloidal material in the molasses required about three times as much of the dye for electrical neutralization as did the raw sugar. The molasses which was very dark in color contained of course much more colloidal material than the raw sugar. It was not determined whether the content of colloidal material varied in the same proportion as the amount of methylene blue required. Since the presence of different electrolytes and a difference in reaction modifies the electrical neutralizing power of colloidal material, as has been shown above, an exact proportion between the two quantities should not be expected.¹

6. Electrokinetics of Barium Sulphate

A study of the electrokinetic behavior of precipitates will undoubtedly be of great value where a control of certain factors such as the size of crystals, dispersion or aggregation are desired. As this subject will receive a more detailed discussion later only one example will be given here.

TABLE VI

The electrical charge of BaSO₄ when formed with an excess of K₂SO₄ and of BaCl₂ and the pH of the supernatant solution

| K ₂ SO ₄ | c.c. 0.1 N BaCl ₂ | μ /sec. 1 volt cm. | P. D. millivolts | pH |
|--------------------------------|---------------------------------|---------------------------|---------------------|-----|
| 10.0 | 5.0 | -3.8 | -53.5 | 7.1 |
| 6.0 | 5.0 | -3.0 | -42.3 | 6.9 |
| 5.2 | 5.0 | -1.1 | -15.5 | 6.6 |
| 5.0 | 5.0 | +0.4 | +5.6 | 6.4 |
| 5.0 | 5.2 | +1.6 | +22.6 | 5.2 |
| 5.0 | 6.0 | +2.8 | +39.5 | 5.0 |
| 5.0 | 10.0 | +4.3 | +60.5 | 4.8 |

¹ After the completion of the above work, the methods developed by the author have, at his suggestion, been applied by M. S. Badollet and H. S. Paine, U. S. Bureau of Chemistry, to a quantitative study of the colloidal materials in sugar-house liquors. These investigators found the basic dye, night blue, more suitable for their work than methylene blue. The value of their work is however doubtful for although they make free use of a manuscript, which the author handed over to Mr. Badollet, regarding description of methods and apparatus they appear to have failed to grasp the principles of electrosmosis and cataphoresis. In explaining the adjustment of the apparatus they refer to a point "where the colloidal particles do not show progressive movement toward either electrode" when no current is flowing. What kind of movement they were observing when no current was flowing and what significance such a point could have is difficult to say. M. S. Badollet and H. S. Paine: *Int. Sugar J.*, 28, 23-28, 97-103, 137-140 (1926).

Different proportions of accurately standardized $N/10$ $BaCl_2$ and K_2SO_4 solutions were rapidly mixed in a total volume of 50 cc. The pH of the distilled water and the two solutions was 6.4. Table VI gives the sign of charge and the electrical migration of the $BaSO_4$ crystals. The last column gives the pH of the supernatant solution colorimetrically determined.

It will be seen that with an excess of the sulphate ions the precipitate is electronegative but with an excess of Ba ions it is electropositive. This must be due to an adsorption of the respective ions. But the association tendency or, to put it otherwise, the solution tension of the Ba and the SO_4 ions must be different because, in equivalent proportions of the reagents, the precipitate is electropositive indicating a slight excess of Ba in the surface layer. $BaSO_4$ is therefore normally, in the absence of surface active anions, electropositive and might be written thus: $(BaSO_4)_zBa_x$, where z is very small.

That the change of the sign of charge on the crystals actually is due to an association of one ion in excess of the other is evident from a corresponding displacement in the pH of the solution. The displacement to the acid side with an excess of $BaCl_2$ is more pronounced than the displacement to the alkaline side with an excess of K_2SO_4 . Why the adsorption of Ba ions should increase the H ion concentration in the solution and why the adsorption of the SO_4 ions should have the opposite effect is easily explained. The adsorbed Ba ions attract an equivalent number of anions which surround the crystal forming the outer ionic layer which, in this case, is electronegative. If the attracted anions consisted exclusively of the Cl ions of the $BaCl_2$ the pH of the outside solution would be unaffected. But the Cl ions are displaced by the more active OH ions of the water resulting in the formation of a trace of HCl in the solution. Similarly, the adsorption of the SO_4 ion attracts an equivalent of cations forming, in this case, an electropositive outer ionic layer. Now it is well known from studies of base exchange that the H ion has a strong displacing power. The H ions of the water displace partially therefore the K ions of the K_2SO_4 with the result that a trace of KOH is formed in the outside solution. This leads to the conclusion that electronegative materials or acidoids must have a higher H ion concentration in a layer near the surface than that of the outside solution. Conversely electropositive materials or basoids must show a lower H ion concentration at the surface. That acid soils and peat show a greater acidity to litmus paper than their water extracts has often been observed.¹ By removing the liberated base by continued leaching of $BaSO_4$ with a K_2SO_4 solution and by a subsequent treatment with a strong chloride solution, an exchange acidity similar to that of soils should be developed.

The above property of $BaSO_4$ may be assumed to be general to a greater or lesser degree for all precipitates. It is improbable that the solution tension of the anions and cations in the crystal lattice is ever exactly the same but varies with the hydration, the diffusibility and other properties of the ions. The fact that precipitates of the same material vary greatly in their

¹ Mattson: *Kolloidchem. Beihefte*, 14, 227 (1922).

behavior is undoubtedly due to slight differences in composition. Such differences might be expressed by the general formulas $(BA)_z B_x$ or $(BA)_z A_x$, depending upon the nature of the material and the conditions under which it is formed. The quantity z may be chemically insignificant but very important as a factor governing the physical character of the material.

7. The Electrokinetics of Certain Soluble Electrolytes

In the case of certain soluble electrolytes the effect of the unequal solution tension of the two ions in the crystal lattice shows itself in a striking manner. Salts of highly hydrated cations and complex polyvalent anions such as the phosphate and ferrocyanide of sodium form, when dissolved, a transient turbidity. A crystal of the ferrocyanide when placed in water and viewed through the microscope fairly appears to explode. Little chips of crystals break away as if repelled by a considerable force and pass only very gradually in solution. These crystal chips carry a very high electronegative charge as determined cataphoretically. By shaking a few crystals of the ferrocyanide with water a transient suspension was formed and, by working rapidly, the cataphoretic movement of the particles could be determined before solution was completed. The particles migrated toward the anode with the extraordinary velocity of 8.4 microns per second corresponding to an electrokinetic potential of 117 millivolts.

The fact that the ferrocyanide crystals break up in water into small fragments before dissolving must be due to this very high electronegative charge which is developed on their surface. This charge is the result of the diverging tendencies of the two ions; the Na^+ ion to diffuse into the water and the $Fe(CN)_6^{4-}$ ion to remain attached to the crystal lattice forming a micelle which might be represented by the formula: $[(Na_4 FeCy_6)(FeCy_6)_4]_4 Na_4^+$. The surprising slowness with which the crystal fragments dissolved, considering the high solubility of the salt, is probably due to the layer of the ferrocyanide ions impeding the outward diffusion.

If the breaking up of the ferrocyanide crystals in water into small fragments is due to a greater solution tension of the Na ions, then this breaking up ought to be prevented by increasing the osmotic pressure of the Na ions by adding a sodium salt of a weakly adsorbed anion. By adding NaCl to the water before the addition of the ferrocyanide it was found that the latter dissolved "normally" without the formation of any turbidity, thus verifying the above conclusions. The presence of an excess of Na ions reduced the diffusion of this ion from the surface of the ferrocyanide and, the Cl ions not being appreciably adsorbed, the P.D. of the double layer did not assume the above high magnitude but remained within the limits of stability of the crystals.

This behavior of a soluble electrolyte to undergo a crystal dispersion before solution takes place will be met with only where the solution tension of the two ions differs greatly as in the case of compounds in which one of the ions has a tendency to become heavily hydrated, i.e. to be strongly adsorbed by the water, while the other ion is strongly attracted and ad-

sorbed by the solid surface. Foremost among the former ions are the alkali cations of low atomic weight and volume such as Na and Li which, because of their small size and the resulting strong electric field, attract and adsorb the water molecules most strongly as pointed out by von Hevesy¹ and by Wiegner and Jenny.² Among the strongly adsorbed ions are the complex and polyvalent ions and notably the OH ions. The transient turbidity formed when NaOH is dissolved is probably due to this tendency of the OH ion and is to be explained as was done in the case of the ferrocyanide. The ions which cause a dispersion of their own crystals before the latter dissolve are therefore the same ions which, when added to a suspension of an insoluble material, cause the highest degree of dispersion provided of course that the suspended material has the same sign of charge as that of the most strongly adsorbed ion. Thus the electronegative clay is most readily dispersed by the hydroxide, phosphate and ferrocyanide of sodium while the electropositive ferric hydroxide is most efficiently flocculated by these electrolytes.

8. Conclusion

In conclusion to the above work a brief definition of the conditions which lead to a potential difference at the interface of in-water-suspended materials will be given. Two forms of electrokinetic potential may be recognized as follows: (1) dissociation potential and (2) adsorption potential. The former results from an unequal diffusibility or an unequal solution tension of the ions in the material itself while the latter is formed through an unequal adsorption of ions foreign to the material but present in the solution.

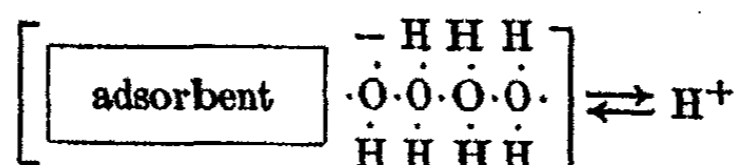
A dissociation potential difference is formed by dispersed materials when one of the ions is diffusible and when the other ion, because of its complexity is nondiffusible or when, because of its low solution tension it remains associated with the molecules of the solid and becomes by virtue of this association a nondiffusible ion. The proteins in combination with acids and bases: $[R.COO^-]Na^+$ and $[R.NH_3^+]Cl^-$ and the oxychloride of iron: $[(Fe_2O_3)_x Fe_2O_2^{++}]_2 Cl^-$ may be mentioned as examples of this type of materials. A dissociation potential is also formed by electrolytes in which both ions are diffusible but possess a different solution tension. Examples of this type are $[(BaSO_4)_x Ba^{++}]SO_4^{--}$ and $[(Na_4FeCy_6)_x FeCy_6^{--}]_4 Na^+$. The sign of charge will be that of the ion with the lowest solution tension. If the difference in tension of the two ions is small as in $BaSO_4$ the charge may be reversed by adding an excess of the ion having the highest tension.

While the dissociation potential may be of either sign of charge, the adsorption potential appears to be always electronegative in aqueous suspensions. The fact that the great number of insoluble and chemically inert substances charge themselves electronegative in water and in solutions of ordinary electrolytes might be explained by considering the chemical nature of the water itself. Since the electrokinetic potential depends upon the most minute

¹ Kolloid-Z., 21, 129 (1917).

² Abstracts Proc. First Int. Congress Soil Science, Second Commission, 40 (1927).

concentrations of ions, water must, for the subject here dealt with, be looked upon as an electrolyte. In the second place water is an ampholyte of the most ideal type since, by dissociation, an equal number of H and OH ions are formed. One of these ions, the OH, has been shown to be one of the most strongly adsorbed ions.¹ Now it is generally assumed that the water molecules, or rather groups of associated water molecules, arrange themselves in an oriented position at interfaces due, probably, to an inequality in the strength of the electric fields at phase boundaries. This means that adsorbed water is structurally different from ordinary water in which the molecules have a random distribution. The question arises: is the adsorbed water also chemically different from ordinary free water? If groups of associated water molecules are electrical bipoles and if the polar orientation is such that the OH ions (and anions in general) are attracted toward the interface then it follows that adsorbed water must be more acidic than water in the free condition. The fixation of the OH ions at the interface leads to the liberation of a proportionally greater number of H ions, which, because of electrostatic forces, are held in the form of an outer layer surrounding the adsorbent. This may be represented by the following scheme:



This would account for the sign of charge of the great body of very different materials (acidoids) which in water charge themselves electronegative. It would also account for the often observed fact that these materials show a higher H ion concentration at their surface than that of the surrounding solution. Further, since the H ions may be displaced by other cations, the source of the acid liberated by the neutral salt treatment is also accounted for. The adsorption of water weakens its basic and strengthens its acidic properties and the adsorbed water exhibits therefore the character of an acid.

The adsorption potential must be looked upon as being superimposed upon the dissociation potential. The sign of charge is determined by the algebraic sum of both. This conception of the mechanism of the two potentials explains several observations which would otherwise be difficult to account for: All materials which by dissociation charge themselves electropositive may be charged electronegative by increasing the OH ion concentration. As examples of such materials may be mentioned the proteins, the colloidal basic dyes, the metallic oxides and barium sulphate. All of these are therefore ampholytoids. Materials which remain electropositive independent of the pH (basoids) are unknown. A great number of materials are always electronegative (acidoids) retaining this charge independent of the pH. Not even the trivalent cations appear to be able to change the sign of charge of these materials. The change in sign of charge of clay brought about by the addition of AlCl_3 has been

¹ Mattson: Kolloidchem. Beihefte, 141, 227 (1922).

shown to be due to the products of hydrolysis, i.e. to the oxychloride, and the resulting positive charge is evidently due to a dissociation of this complex. The adsorption potential appears therefore to be strictly electronegative as a consequence of the attraction of the anions (OH and others) to the interfacial side of the adsorbed water. The negative charge of the noble metals which, because of their low solution tension, would be expected to be electropositive, as pointed out by Freundlich,¹ is explained by this adsorption. The observation made by Freundlich that the electrokinetic potential does not always parallel the Nernst potential, has been explained by him, and is further made more comprehensible by the above deductions.

The above work was performed in the Bureau of Soils of the United States Department of Agriculture.

Summary

An ultramicroscopic cell which permits a rapid determination of the cataphoretic movement of colloidal particles has been described.

Several applications of cataphoresis have been given as follows:

(1) The electrical neutralization of clay suspensions by salts of aluminum. The experiment showed that it is the products of hydrolysis of these salts rather than the trivalent cations which are active and that an adjustment of the pH to a value of about 5.2 is essential for the highest degree of efficiency.

(2) The electrical neutralization of clay by the basic dye methylene blue in the presence of different anions and cations showed that the isoelectric ratio $\left(\frac{\text{methylene blue}}{\text{clay}}\right)$ was increased by the former and decreased by the latter ions, the effect increasing with the valence.

(3) The quantities of methylene blue required to neutralize the electro-negative proteins in milk decreased with the acidity (i.e. increased with the freshness) of the latter. The electrical neutralization of the colloidal materials in raw sugar and in molasses indicated a proportionality between the neutralizing power and the quantities of colloidal material present.

(4) A study of the electrokinetic behavior of BaSO₄ showed that this material is, by itself and in the presence of an excess of Ba, electropositive while in the presence of an excess of SO₄ it is electronegative. The electropositive condition causes a decrease and the electronegative condition causes an increase in the pH of the solution. The former phenomenon was explained on the basis of a difference in solution tension of two ions and the latter by assuming an adsorption of the OH and H ions of the water respectively.

(5) The behavior of certain soluble electrolytes, such as the ferrocyanide of sodium, of forming a turbid suspension before dissolving was cataphoretically investigated. The crystal chips which in water break away from the larger crystals were found to carry an extraordinary high electronegative

¹ "Kapillarchemie", 339 (1922).

charge. The great solution tension of the highly hydrated Na ions and the low tension of the tetravalent anion (which is a highly adsorbed ion) was held responsible for this behavior.

In conclusion it was pointed out that all electrolytes may give rise in water to a dissociation P.D. at the phase boundaries, the sign of charge being determined by the solution tension and osmotic pressure of the respective ions. But the cause of the electronegative charge of the great number of inert materials is to be sought in the adsorbed layer of oriented water molecules which apparently attract the anions to the interfacial side of this layer giving rise to an adsorption potential. Adsorbed water is held to be more acidic than free water.

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New Brunswick, N. J.
1928.*

THE PORE SIZE OF COMPRESSED CARBON AND SILICA MEMBRANES¹

BY F. E. BARTELL AND H. J. OSTERHOF

For many purposes the determination of pore size in membranes of colloid and of compressed solid substances is essential. In particular for the calculation of adhesion tensions by the method involving the measurement of the displacement pressure, liquid against liquid, it is necessary to know quite accurately the pore radius of membranes formed by compressing the fine powders used.

Of the methods available for the determination of the radius of capillary tubes, there are three which may be considered suitable for this purpose. These are (1) decrease in vapor pressure of a liquid with the increasing curvature of its meniscus in a capillary tube; (2) the height of ascension or the pressure necessary to prevent ascension of a liquid in a capillary; and (3) the application of the law of Poiseuille to the rate of flow of a liquid through the capillary. The first two methods can be employed for the measurement of the average pore radius of a membrane and in principle are the same as the methods used for a single capillary tube. The third method requires either a knowledge of the number of pores in unit cross-section of the membrane, or the use of a suitable formulation in which this quantity does not enter.

Vapor pressure method: This method is based upon the fact that the vapor pressure above the concave surface of a liquid is less than that above the plane surface of this liquid, and that this pressure decreases with increasing curvature of the surface. For fine capillaries whose radius is essentially equal to the radius of curvature of the meniscus the radius may be calculated from the equation:

$$R = \frac{2S d_1}{d_0 p_0 \log p_0/p_1} \quad (1)$$

where

S = surface tension of the liquid

d_1 = density of saturated vapor

d_0 = density of liquid in pores

p_0 = vapor pressure of liquid en masse

p_1 = vapor pressure in equilibrium with the liquid in the capillary.

¹The material included in this article constitutes a portion of a dissertation presented to the Graduate Faculty of the University of Michigan by H. J. Osterhof, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

A paper based upon the results of the present contribution was presented before the Division of Colloid Chemistry and the Division of Paint and Varnish Chemistry at the 74th meeting of the American Chemical Society, Detroit, Michigan, September 5 to 10 1927.

This formulation was employed by Anderson¹ to measure the pore diameter of the openings in a silica gel. Water, alcohol and benzene gave consistently close results. The diameter of the capillary pores ranged from 2.63 μ to 5.55 μ and the number of pores per unit cross-section of the gel was approximately 10^{12} . Determinations according to Anderson's method were also carried out with silica gel by Patrick.²

Capillary rise formulation: The radius of a capillary sufficiently small may be calculated from the equation:

$$R = \frac{2S}{hdg} = \frac{2S}{Pg} \quad (2)$$

in which

S = surface tension of the liquid

h = height in cm. to which liquid will ascend in the tube

d = density of the liquid

g = gravitational constant

P = pressure in grams per cm². necessary to prevent advance of the liquid in the capillary tube.

The liquids selected should give zero angles of contact with the tube walls.

This method was used by Bechhold³ in his work on ultrafiltration, and was extended by Bigelow and Bartell,⁴ and by Bartell and Carpenter.⁵ In this work the membranes were saturated and then covered with water, and air admitted beneath the membrane from a pressure tank. The pressure was measured at which water was forced out of the pores and air bubbles appeared on the surface of the membrane.

Method based upon application of Poiseuille's law: The radius of a single capillary tube may be determined from the relation:

$$Q = \frac{\pi g P R^4 t}{8 l \eta} \quad (3)$$

where Q is the quantity of liquid of viscosity η flowing in time t through a tube of length l and radius R under a pressure of P grams per cm.² The average pore radius of a membrane containing n capillaries per sq. cm. may be obtained from this same relation if the right hand member of the equation be multiplied by n . This formulation has been applied to test the permeability of various membranes. Bigelow⁶, working with collodion membranes, Bartell⁷ with porcelain discs and copper ferrocyanide membranes, Duclaux

¹ Z. physik. Chem., 88, 191 (1914).

² Inaug. Diss. Göttingen (1914).

³ Z. physik. Chem., 64, 328 (1908).

⁴ J. Am. Chem. Soc., 31, 1194 (1909).

⁵ J. Phys. Chem., 27, 252 (1923).

⁶ J. Am. Chem. Soc., 29, 1675 (1907).

⁷ J. Phys. Chem., 15, 659 (1911); 16, 318 (1912).

and Errera¹ with nitrocellulose and cellulose acetate membranes, have shown that the rate of flow of different liquids is proportional to the pressure and inversely proportional to the thickness of the membrane and the viscosity of the liquid.

On the assumption that these membranes are composed of small capillary pores whose length is equal to the thickness of the membrane, the average pore radius has been determined by Guérout,² Hitchcock,³ and Duclaux and Errera.⁴

Review of the methods based on capillary rise and on the law of Poiseuille: Both methods have been criticized by different writers on the ground that the formulations are not applicable to the cases in point. Hitchcock has questioned the results obtained by Bartell and Carpenter with the capillary pressure method. Gurchot,⁵ in a superficial criticism has stated that, insofar as permeability measurements are concerned, the use of Fick's diffusion equation would be preferable to that of Poiseuille's law. Because of these differences in opinion it seemed advisable to study these two methods rather carefully and determine their applicability for the measurement of membrane pore diameters.

Capillary rise method: The formulation for capillary rise, as stated by Lord Rayleigh,⁶ is

$$2 a^2 = \frac{2S}{gd} = r h \left(1 + \frac{1r}{3h} - 0.1288 \frac{r^2}{h^2} + 0.1312 \frac{r^3}{h^3} \right). \quad (4)$$

In the case of water the error involved in disregarding all but the first term in the right hand member is about 2.2 per cent when $r = 0.1$ cm. and 0.02 per cent when $r = 0.01$ cm. For radii smaller than 0.01 cm. it is sufficiently accurate to employ the formula

$$R = \frac{2 S \cos \theta}{d h g} = \frac{2 S \cos \theta}{P g} \quad (5)$$

Similar to the capillary rise method is the method of Cantor⁷ and Jaeger⁸ in which is measured the pressure required to detach a bubble of air from the mouth of a capillary tube placed under the surface of a liquid. This method is essentially the same as that employed by Bartell and Carpenter in their work with collodion membranes. Schrödinger⁹ proposes for this method the relation:

$$2 a^2 = r h \left(1 - \frac{2}{3} \frac{r}{h} - \frac{1}{6} \frac{r^2}{h^2} \right). \quad (6)$$

¹ Kolloid-Z., 38, 54 (1926).

² Compt. rend., 75, 1809 (1872).

³ J. Gen. Physiol., 9, 755 (1926).

⁴ Kolloid-Z., 38, 54 (1926).

⁵ J. Phys. Chem., 30, 83 (1926).

⁶ Proc. Roy. Soc., 92 A, 184 (1915).

⁷ Wied. Ann., 47, 399 (1892).

⁸ Z. anorg. allgem. Chem., 101, 1 (1917).

⁹ Ann. Physik, (3) 46, 413 (1915).

As in the previous equation, for radii smaller than 0.01 cm. all terms beyond the first may be disregarded and the two equations are then the same.

In order that equation (5) may properly be employed for the determination of pore radii of collodion and compressed solid membranes, it is necessary to know three factors: the value of the contact angle, the possibility of variation in surface tension of the liquid as the pore radius approaches molecular dimensions, and the effect of the shape of the pores on capillary rise. The determination of the contact angle offers no particular difficulties. In another article we shall detail the method employed for the measurement of this angle between liquids and finely powdered solids.

In regard to the variation in surface tension with decrease in pore radius, Freundlich¹ states that this value will vary when the radius falls within the order of magnitude of the radius of molecular attraction, but that the variation cannot be great since the falling off of molecular attraction with distance is extremely rapid. Patrick and Eberman² evaluating their experimental results by an extended series of assumptions and approximations are led to the belief that the surface tension of a liquid is a function of the curvature. Bakker,³ from theoretical considerations concludes that the surface tension is completely independent of the curvature of the surface layer. In a series of articles,⁴ he arrives at values for the thickness of the surface layer (i.e., the layer whose properties differ from those of the substance in bulk) which range from one $m\mu$ upward. The thickness of this surface layer increases with rise in temperature until at the critical temperature it becomes extremely large.

Edser⁵ by means of the inverse eighth power law of molecular attraction derived by him calculated that "of the energy which represents the surface tension of a liquid, 94 per cent is located in the surface layer one molecular diameter in thickness." Experimental work by Rayleigh⁶ and Langmuir⁷ and others has given values for the thickness of the surface layer varying from less than one up to four or five $m\mu$. If, in accord with these values, the thickness of the surface layer is considered to be 5 $m\mu$ (i.e. from five to ten molecular diameters) then the minimum diameter of a capillary tube in which the same behavior can be expected as from the liquid in bulk will be between 10 and 15 $m\mu$. Consequently, the surface tension of a liquid may be considered as constant in capillary tubes whose diameter is greater than this minimum value.

Terzaghi⁸ has made calculations on the increase in surface tension of liquids contained in micropores. He derived two equations for this change in surface

¹ "Colloid and Capillary Chemistry", p. 46.

² J. Phys. Chem., 29, 220 (1925).

³ Z. physik. Chem., 104, 29 (1923).

⁴ Z. physik. Chem., 86, 129 (1918) and onwards.

⁵ Fourth Brit. Assoc. Advancement Sci. Colloid Report, p. 94 (1922).

⁶ Phil. Mag., (5) 48, 331 (1899).

⁷ J. Am. Chem. Soc., 39, 1869 (1917).

⁸ Colloid Symposium Monograph, 4, 58 (1926).

tension, the first being based on the assumption that decrease in specific volume is caused by lowering the temperature at constant pressure, and the second on the assumption that the increase in density of the liquid in micropores is due to raising the pressure at constant temperature and that surface tension is proportional to the total internal pressure.

Basing his calculations on the pressure of compression of water by charcoal and its consequent decreased specific volume, as reported by Harkins and Ewing,¹ Terzaghi obtained a surface tension value of 600 dynes per cm. with the first equation and 200 dynes per cm. with the second. Although not in close agreement these values would lead to the conclusion that the surface tension of the water contained in very fine pores is very much greater than in its normal condition. These conclusions, however, are based entirely upon the interpretation which Harkins and Ewing place upon their experimental data on the variation of apparent density of charcoal in different liquids, an interpretation open to very serious criticism. They concluded that the adhesional pressure between carbon and liquids is more than 20,000 atmospheres in excess of the internal pressures of the liquids, and that in the case of water the specific volume is approximately 0.75.

This hypothesis of a very high adhesional pressure was apparently supported by the work of Lamb and Coolidge,² who concluded that the net heats of adsorption of liquids on charcoal are merely the heats of compression under high pressure and that apparently liquids are all attracted by charcoal with substantially the same force—the absolute value of this attractive force being about 37,000 atmospheres. Later, however, Coolidge,³ decided that this conception was erroneous. Because of the fact that the capacity of the adsorbent is decreased with rise in temperature he considered that in none of the cases studied was it necessary to assume an excess pressure of compression as high as 500 atmospheres. Recently Howard and Hulett,⁴ determined the apparent densities of various samples of carbon by the use of helium gas, and found values higher than those obtained by Harkins with even the most compressible liquids. These results make it appear almost certain that the variations in the density of charcoal observed by the latter are due merely to the difference in depth of penetration of the immersion liquids, and not to the presence of a highly compressed liquid film of greater than normal density.

Finally, work by the authors on adhesion tensions solid-liquid has convinced us that the adhesional pressure between carbon and water is at least 1000 atmospheres less than the internal pressure of water, while even in the case of the most strongly adsorbed organic liquids, the excess of adhesional pressure above the internal pressure of the liquids is not more than 5000 atmospheres. It thus seems most probable to us that the values stated by

¹ Proc. Nat. Acad. Sci., 6, 49 (1920); J. Am. Chem. Soc., 43, 1787 (1921).

² J. Am. Chem. Soc., 42, 1146 (1920).

³ J. Am. Chem. Soc., 48, 1795 (1926).

⁴ J. Phys. Chem., 28, 1082 (1924).

Harkins for the pressure of compression and increase in density of an adsorbed liquid are very much too great. Consequently, the increase in surface tension calculated by Terzaghi and based on Harkins' data is also much too large; the true values differ probably very little from the normal surface tension, and even this variation undoubtedly occurs within the molecular limits previously discussed.

As to the effect of the shape of the pores on capillary rise, Schultze¹ has compared the capillary rise in tubes of circular cross section with that in tubes of elliptical and irregular cross section. He quite naturally found that for a given cross sectional area the rise was greater in the non-circular tubes. In the case of collodion and similar membranes the pores are probably circular or only slightly elliptical in cross section. In compressed solid membranes, if the particles were spherical the interstices would quite probably be triangular; with irregularly shaped particles, the pores will be of all conceivable shapes. It will occasion no very great error, however, to assume that the effective average of thousands of such pores superimposed upon each other will be a pore whose cross-section approximates an ellipse of comparatively small eccentricity.

Two methods are suitable for the treatment of such an elliptical pore and the determination of its effective radius, if the major semi-axis is less than 0.01 cm. The first is the use of the well known equation:

$$P = S(1/R_1 + 1/R_2),$$

for which an approximate solution can be obtained only in certain special cases² even if the surface is one of revolution. Values calculated with this may serve, however, as a first approximation. The second method is the use of the equation:

$$r = 2 A/l,$$

where A is the cross-sectional area and l the circumference of the pore.³ Values of the effective radii as determined by these methods are compared in Table I, where a and b are the major and minor semi-axes of the ellipse and e the eccentricity. R_a equals $\sqrt{\frac{\pi a b}{\pi}}$, and is the radius of a circle having the same area as the ellipse.

R_b equals the radius of a circle giving the same capillary rise as calculated from $P = S(1/R_1 + 1/R_2)$, where R_1 and R_2 are taken as a and b respectively, and

R_c equals the radius of a circle giving the same capillary rise as calculated from $r = 2 A/l =$

$$4 a \int_0^{\pi} \frac{2 \pi a b}{\sqrt{1 - e^2 \sin^2 \Phi}} d\Phi,$$

the denominator being evaluated from elliptical integral tables.

¹ Kolloid-Z., 36, 65; 37, 10 (1925).

² Ferguson: Trans. Faraday Soc., 17, 375 (1922).

³ Bouasse: "Capillarité", p. 163; Desains: Ann. Chim. Phys., (3) 51, 385 (1857); Richards and Carver: J. Am. Chem. Soc., 43, 827 (1921).

TABLE I
Effective Radii of Elliptical Tubes

| a | b | e | R _a | R _b | R _c |
|--------|--------|-------|----------------|----------------|----------------|
| 1.25 R | 1.00 R | .600 | 1.118 R | 1.111 R | 1.110 R |
| 1.50 | 1.00 | .745 | 1.224 | 1.200 | 1.188 |
| 2.00 | 1.00 | .866 | 1.414 | 1.333 | 1.297 |
| 4.00 | 1.00 | .968 | 2.00 | 1.60 | 1.46 |
| 9.00 | 1.00 | .994 | 3.00 | 1.80 | 1.54 |
| 100. | 1.00 | .9999 | 10.00 | 1.98 | 1.5708 |

It is apparent from this table that for values of the eccentricity that are not too large, the calculated effective radii R_b and R_c are substantially the same and that also they do not differ markedly from the radius of a pore having the same cross-sectional area.

Method based upon Poiseuille's law: The average pore radius of a membrane containing *n* capillary pores normal to its cross-section is given by the relation:

$$R = \sqrt[4]{\frac{8 l \eta Q}{n \pi g P t}}$$

We shall now examine rather carefully the factors which might be sources of error and invalidate the use of a method based on this equation and attempt to determine the conditions under which this method should be correct.

(a) Although *n*, the number of pores, cannot be determined directly, the equation (as will be seen later) can be so revised that this value does not enter in the calculations.

(b) The length of the pores in a collodion or nitrocellulose membrane is customarily taken equal to the thickness of the membrane. The mechanism of the preparation of these membranes, as described by Bartell and Van Loo,¹ is such, that this assumption appears justified. In the case of membranes formed by compressing a powdered solid, however, the length of the pores must be greater than the thickness of the membrane. Working with a bundle of asbestos filaments, Guérout calculated from microscopic observations a pore cross section of 0.0024 sq. mm. while rate of flow experiments gave 0.0025 sq. mm. With a layer of compressed sand the calculated mean cross-section of the capillary pores was 0.0004 sq. mm. while experiment gave 0.0002 sq. mm. Hitchcock accounts for this deviation by assuming that in the case of spherical grains the length of the capillaries ought to be greater than the thickness of the sand membrane in the ratio of π to 2. In the case of carbon and silica membranes we have felt justified in multiplying the thickness of the membrane by the factor $\pi/2$ in order to obtain the average length of the capillary pores.

(c) The possibility of slippage between liquid and pore walls is discussed by Bingham.² Summing up the large amount of experimental work

¹ J. Phys. Chem., 28, 161 (1924).

² "Fluidity and Plasticity", p. 29-35 (1922).

on this subject he concludes that, whether the liquid wets the solid or not, there is no measurable slipping, at least so long as the flow is linear. Even in the case of mercury and glass where the liquid wets the solid so slightly that the angle of contact is around 140° , Warburg¹ proved that slipping did not occur.

Recent work by Tammann and Hinnuber² appears to prove that a considerable slippage occurs for mercury in capillaries of glass and other materials. Employing carefully cleaned and amalgamated capillary tubes they found a value three times as large as the value hitherto determined for capillary tubes of various materials.

(d) Unless the rate of flow is very slow it is necessary to apply a correction for the loss in kinetic energy of the liquid. Poiseuille's formula then becomes:

$$\eta = \frac{P R^4 \pi g t}{8 Q l} - \frac{m d Q}{8 \pi l t}$$

where d is the density of the liquid and m a constant. By means of a rigorous theoretical treatment, Boussinesq³ has found $m = 1.12$ while Knibbs⁴ calculating from Poiseuille's experimental data found a mean value of $m = 1.13$. The corrected expression for the radius (and assuming n the number of pores in the membrane) is:

$$R = \sqrt[4]{\frac{8 l \eta Q + \frac{1.12 d Q^3}{\pi t}}{n \pi g P t}}$$

A simple calculation shows that for a membrane 0.01 cm. in thickness which contains only 1000 pores per square cm. the neglect of this correction will involve no more than 0.01 per cent error, when the rate of passage of water is not greater than 0.001 cm.³ per second. Although irregularities in the bore of these pores will have a very great influence in altering the amount of this correction, nevertheless in the experimental work in all cases the number of pores in unit area has been so much greater and the rate of passage of liquid so much slower than in the limits stated above, that the correction will undoubtedly still remain negligible.

(e) Any variation from a circular cross section will also affect the rate of flow. We shall consider, as in the discussion of the capillary rise method, that no very great error will be caused by the assumption that the average pore is approximately elliptical in cross-section. It can then be treated by the expression given by Rucker⁵ where R_d is the radius of a tube of circular

$$R_d^4 = \frac{2 a^3 b^3}{a^2 + b^2}$$

¹ Pogg. Ann., 140, 367 (1870).

² Z. anorg. allgem. Chem. 167, 230 (1927).

³ Compt. rend., 113, 9, 49 (1891).

⁴ J. Proc. Roy. Soc. N. S. Wales, 29, 77 (1895).

⁵ Phil. Trans., 185 A, 438 (1894).

cross-section which would give the same rate of flow as an elliptical tube for which a and b are the major and minor semi-axes. Table II compares this value with the mean effective radii determined by capillary rise formulations.

TABLE II
Rate of Flow in Tubes of Elliptical vs. Circular Cross-Section

| a | b | R_a | R_b | R_c | R_d |
|--------|--------|---------|---------|---------|---------|
| 1.25 R | 1.00 R | 1.118 R | 1.111 R | 1.110 R | 1.112 R |
| 1.50 | 1.00 | 1.224 | 1.200 | 1.188 | 1.201 |
| 2.00 | 1.00 | 1.414 | 1.333 | 1.297 | 1.337 |
| 4.00 | 1.00 | 2.00 | 1.60 | 1.46 | 1.65 |

It is evident that for elliptical cross-sections of moderate eccentricity the agreement between the effective radii calculated by these different methods is quite close.

(f) It is also desirable to know the minimum radius and minimum length of a capillary tube for which Poiseuille's formulation holds without appreciable correction. Although the smallest tube employed by Poiseuille had a radius of 0.0007 cm. and a length of 0.125 cm., this does not by any means represent the minimum value for these dimensions. The relations expressed in the formulation should hold down to the lowest limits at which a liquid still possesses its normal properties; i.e. where its viscosity is the same as that of the liquid in bulk. Previous considerations have shown that the minimum diameter of a tube whose central channel will contain liquid satisfying these requirements is probably not greater than twelve to fifteen $m\mu$. It may indeed be less than this, if no more than two or three molecular layers are firmly held by the solid, since the movement of the liquid is tangential to the surface of the pores. This would give a lower limit to the radius of the capillary of between 0.5 to 1.0×10^{-6} cm. In contradiction to this view, however, Terzaghi derived for the viscosity of water in narrow openings the empirical formula:

$$\eta' = \eta \left(1 + \frac{6.02 \times 10^{-43}}{r^3} \right) \text{ to } \eta \left(1 + \frac{2.42 \times 10^{-43}}{r^3} \right),$$

where η is the normal viscosity and η' the viscosity in a slit of width $2r$ cm. According to this, Poiseuille's formulation would be valid down to a pore radius of 10^{-5} cm.; with decrease in pore radius the apparent viscosity would increase rapidly until at a radius of 1.0×10^{-6} cm. its value would lie between 10^5 and 10^6 times the normal value. Apparently we may consider a radius of 10^{-5} cm. as a safe lower limit; without further experimental data the employment of this method for the determination of smaller radii remains a debatable question. Thus the values for the pore radii of collodion membranes as determined by Hitchcock,¹ which range from 2.2 down to 0.27×10^{-6} cm. (the latter being only six molecular diameters) are of questionable significance.

¹ J. Gen. Physiol., 9, 759 (1926).

The minimum length for correct determinations with a capillary tube is dependent upon the radius. In Poiseuille's experiments the ratio R/l varied between 22×10^{-6} and 1046×10^{-6} without appreciably affecting the values determined for the viscosity. We may consider, then, that conditions will be satisfactory if the length of the pore is more than one hundred times its radius. In all reported work on membrane pore size and in our own experimental work this condition has been satisfactorily met.

(g) As regards the action of a curved instead of a straight capillary pore Edser¹ states that the inner surface of the tube will be subjected to tangential forces parallel to the direction of flow, and that these forces will have no tendency to set the tube in motion laterally (i.e. to exert a pressure perpendicular to the walls of the tube).

W. R. Dean,² in an article: Note on The Motion of Fluid in a Curved Pipe, contributes to the theory of the steady motion of a liquid through a tube of circular cross-section which is coiled in a circle. His theoretical results agree well with experiments on this type of motion by Eustice,³ but are still of such a qualitative nature as to prevent their use in the calculation of the necessary corrections. He states: "It is known that to cause a given rate of flow a larger pressure gradient is required in a curved pipe than in a straight one, the difference being considerable even when the curvature is small.—There is not a constant pressure gradient as there is in the case of flow through a straight pipe."

(h) Finally, there is the possibility of eddy or turbulent flow, due to high velocity, change in pore size within the length of the pore or change in direction of the pore. For a regular capillary tube, Reynolds⁴ found that the maximum mean velocity in centimeters per second for which linear flow could still exist is given by the relation:

$$V = \frac{1000 \eta}{d R}$$

For a pore 10^{-6} cm. in radius this maximum velocity for water would be approximately 10^6 centimeters per second. Abrupt changes in pore size or direction would tend to promote turbulent flow, but by keeping the rate of flow low this possibility would be obviated.

Three of the factors discussed above, which bear on the applicability of the methods for pore size determinations based upon capillary rise and upon Poiseuille's formulation, do not admit of very accurate treatment. These three factors are pore length, pore curvature and pore shape. They have, in fact, a more or less direct bearing upon several of the other factors. The term $\pi/2$ (used in b) is unquestionably somewhat larger than is necessary in the calculation of effective pore length. This term will, however, serve

¹ "General Physics", p. 417 (1922).

² Phil. Mag., (7) 4, 208, (1927).

³ Proc. Roy. Soc., 85 A, 119, (1911).

⁴ Phil. Trans., 174, 935 (1883).

approximately to compensate for two differences in value arising from the fact that the flow is through curvilinear or sinuous pores rather than through straight tubes. These corrections which are more or less mutually inclusive may be stated as: (1) The increased length of the stream lines of a liquid flowing through a curved pore, and (2) the larger pressure gradient required to cause a given rate of flow in a curved pore than in a straight one. Inaccuracies due to pore shape, different from those discussed, are probably within the limits of experimental error. It is felt, therefore, that the use of the term $\pi/2$ is justified and that this term will tend to take care of all three factors mentioned without involving errors of appreciable magnitude.

Experimental

Bearing in mind the conditions above mentioned we determined the pore sizes of compressed carbon and silica membranes by the two methods in order to institute a comparison between them, and also to obtain values in which we might have some degree of confidence.

Capillary Rise Method: In employing this method for the determination of pore size of collodion membranes Bartell and Carpenter measured the pressure necessary to force liquid out of the previously wetted membrane and cause the formation of air bubbles on its surface. In the case of membranes formed by the compression of finely powdered solids a somewhat different application of the method was found suitable. Powdered material of quite uniform particle size was compressed by a hydraulic press in brass displacement cells in a manner similar to that employed for the determination of displacement pressures of one liquid by another.

In effect, that which was to be measured was the displacement of air by liquids instead of one liquid by another.

One end of the displacement cell was connected through a pressure gauge with a compressed air container; the compressed solid in the other end of the cell was wetted with the liquid, this liquid extending out from the cell into an indicator capillary. When the cell had been connected the liquid commenced to advance inward through the fine capillary interstices. The opposing air pressure was built up by successive small increments until finally an equilibrium point was reached where the liquid, as shown by indicator gauges on both ends of the cell no longer advanced but remained stationary in the pores. This pressure was considered as the pressure necessary to prevent movement of the liquid in the tube and would be identical with the pressure which would be exerted if the liquid had risen to its equilibrium height in a tube of the same dimensions.

With the carbon membranes benzene, chloroform and toluene were employed since these liquids give zero contact angles with the solid. With the silica membranes we employed water and benzene for the same reason. Since the contact angle is zero the evaluation of the radius then follows from the equation:

$R = \frac{2S}{d h g} = \frac{2S}{Pg}$, where S represents the surface tensions of these liquids at 25°C , P is the equilibrium pressure in grams per cm.^2 and g is taken as 981 dynes per gm. The values for the radius as calculated from this equation are given in Table III.

TABLE III
Determination of Pore Radius
Method based on Capillary Formulations

| Temp. = 25°C . | | $R = \frac{2S}{hdg} = \frac{2S}{Pg}$ | | | |
|--------------------------------|------------|--------------------------------------|------------------|-------|------------------------|
| Solid | Liquid | Surface tension S | Grams press. P | | Radius $R \times 10^6$ |
| Carbon (2500 lb.) | Benzene | 28.25 | 6200 | 9.29 | |
| | | | 6220 | 9.26 | |
| | | | 6200 | 9.29 | |
| | | | 6200 | 9.29 | |
| | | | 6200 | 9.29 | 9.29 ave. |
| Carbon | Chloroform | 26.63 | 5800 | 9.36 | |
| | | | 5800 | 9.36 | 9.36 " |
| Carbon | Toluene | 27.70 | 6100 | 9.26 | |
| | | | 6100 | 9.26 | 9.26 " |
| Silica (3000 lb.) | Water | 72.08 | 699 | 210.2 | |
| | | | 697 | 210.8 | |
| | | | 697 | 210.8 | 210.6 " |
| Silica | Benzene | 28.25 | 271 | 212.5 | |
| | | | 277 | 208.0 | |
| | | | 276 | 208.7 | 210 " |

Method based on Poiseuille's formulation: As has been seen, the mean radius of a collection of n capillary tubes where n is definitely known, is given by the equation:

$$R = \sqrt{\frac{8 l_0 \eta Q}{n \pi g P t}}$$

Since in these membranes, however, n cannot be directly evaluated, it is necessary to revise this equation in such a manner that n need not be determined.

The quantity of liquid, Q , which passes through the entire cross-section of the membrane in time, t , is given by:

$$Q = \frac{n \pi P R^4 g t}{8 l_0 \eta} = \frac{P R^2 g t}{8 l_0 \eta} \times (n \pi R^2)$$

The total pore volume for the entire membrane is equal to $n\pi R^2 l_0$, or:

$$Q = \frac{P R^2 g t}{8 l_0 \eta} \times \frac{V}{l_0},$$

where V equals the total pore volume of the membrane. The expression for the radius then becomes:

$$R = \sqrt{\frac{8 \eta Q l_0}{P V g t}}$$

We have further considered that for a compressed solid membrane the effective pore length is equivalent to $\pi/2$ times the thickness of the membrane. With this final correction the relation which will be employed for the calculation of pore radii is:

$$R = \frac{\pi l}{2} \sqrt{\frac{8 \eta Q}{P V g t}}$$

where

R = the average effective radius of the pore in cm.

l = the thickness of the membrane or, in this case, the interior length of the displacement cell in cm.

η = a constant in dyne seconds per cm.

Q = the volume of liquid forced through cell in cm^3 .

P = the pressure in gms/cm^2 .

V = the total pore volume or the interior volume of the displacement cell minus the volume of compressed solid contained in it in cm^3 .

g = gravitational constant in dynes /gm.

t = the time in seconds for passage of quantity, Q .

The experimental procedure was as follows: the specific gravity of the carbon was determined in benzene, that of the silica in water. Weighed quantities of the powdered solid were thoroughly exhausted by means of a mercury diffusion vacuum pump and then while still under the vacuum were completely wetted with an excess of water. This weighed amount of powder was packed by the hydraulic press in the brass displacement cells as in the previous determination, and connected with a water reservoir under a constant pressure head of mercury or water. The quantity of liquid, Q , forced through the cell by pressure P was measured from time to time over a period of several hours. The experimental data and calculated radii are given in Tables IV-VI. In these tables L is the distance in centimeters between marks on the external portion of the two perforated brass plungers which formed the end of the displacement cell. This distance is measured when the cell

is filled, packed, and in operation. The actual length of the two brass plungers between these marks is 12.60 cm. Subtracting this value from L gives l , which is the interior length of the cell or in other words the thickness of the compressed membrane. The interior volume of the displacement cell, V_0 , is equal to $(1/4) \pi D^2 l$, the diameter of the cell being 1.92 cm. The volume actually occupied by the compressed powdered solid, v , is calculated from the specific gravity of the powder and the weight used to fill the cell. The difference between these two quantities, V_0 and v , is V the total pore volume of the membrane.

Comparison of the two methods: In the determination of the pore radii by Poiseuille's method it is at once observed that the apparent radius decreases with lapse of time from the commencement of the experiment. This fact has been commented upon by others who have used this method for determining membrane permeability and various reasons have been assigned for it. What seems the most reasonable explanation has been given by Bartell,¹ who considers that the decrease in permeability with time and, consequently, the decrease in the calculated radius is caused by a mechanical clogging of the pores by very fine solid particles. This is borne out more particularly by our observations on silica membranes. The first portion of the liquid forced through was rather turbid in appearance; this turbidity decreased with time until finally the liquid was entirely clear. Part of this finely dispersed sus-

TABLE IV
Determination of Pore Radius
Method based on Poiseuille's Formulation

| C. B. under 1500 lbs. pressure Temp. = 23.0°C | | | | | Weight C. B. = 11.00 gm. P = 60 cm. Hg. | | |
|--------------------------------------------------|------|-------|------|-------|--------------------------------------------|------|-----------------|
| L | l | V_0 | v | V | t min. | Q | $R \times 10^6$ |
| 18.90 | 6.30 | 18.24 | 6.71 | 11.53 | 90 | .960 | 11.89 |
| | | | | | 90 | .958 | 11.87 |
| | | | | | 90 | .950 | 11.82 |
| 18.90 | 6.30 | 18.24 | 6.71 | 11.53 | 90 | .950 | 11.82 |
| | | | | | 90 | .950 | 11.82 |
| | | | | | 90 | .945 | 11.80 |
| | | | | | 90 | .940 | 11.76 |
| 18.60 | 6.00 | 17.37 | 6.71 | 10.66 | 90 | .930 | 11.59 |
| | | | | | 90 | .930 | 11.59 |
| | | | | | 90 | .928 | 11.56 |
| | | | | | 90 | .930 | 11.59 |

¹ J. Phys. Chem., 15, 665 (1911).

pension undoubtedly remained within the pores, clogging them and thus giving a smaller mean pore radius. Even in spite of this source of error the agreement between the values determined by the two methods is remarkably close.

TABLE V
Determination of Pore Radius
Method based on Poiseuille's Formulation

| Carbon Black under 2500 lb. pressure Temp. = 23.0°C | | | | | Weight C.B. = 13.00 gm. P = 100 cm. Hg. | | |
|--------------------------------------------------------|------|----------------|------|-------|--------------------------------------------|-------|---------------------|
| L | l | V ₀ | v | V | t min. | Q | R × 10 ⁶ |
| 18.97 | 6.37 | 18.44 | 7.93 | 10.51 | 90 | .800 | 8.90 |
| | | | | | 90 | .750 | 8.62 |
| | | | | | 120 | .820 | 7.81 |
| | | | | | 120 | .785 | 7.64 |
| | | | | | 120 | .750 | 7.46 |
| | | | | | 120 | .750 | 7.46 |
| 18.95 | 6.35 | 18.38 | 7.93 | 10.45 | 90 | .780 | 8.79 |
| | | | | | 120 | .940 | 8.35 |
| | | | | | 120 | .830 | 7.85 |
| | | | | | 120 | .760 | 7.51 |
| | | | | | 120 | .756 | 7.49 |
| | | | | | 120 | .755 | 7.49 |
| 18.80 | 6.20 | 17.95 | 7.93 | 10.02 | 120 | 1.050 | 8.80 |
| | | | | | 120 | .930 | 8.29 |
| | | | | | 120 | .870 | 8.01 |
| | | | | | 120 | .800 | 7.68 |
| | | | | | 120 | .799 | 7.68 |
| | | | | | 120 | .785 | 7.61 |
| | | | | | 120 | .765 | 7.51 |
| | | | | | 120 | .760 | 7.49 |
| 18.96 | 6.36 | 18.42 | 7.93 | 10.49 | 120 | 1.055 | 8.85 |
| | | | | | 120 | .940 | 8.35 |
| | | | | | 120 | .880 | 8.08 |
| | | | | | 120 | .858 | 7.98 |
| | | | | | 120 | .830 | 7.85 |
| | | | | | 120 | .785 | 7.63 |
| | | | | | 120 | .775 | 7.58 |
| | | | | | 120 | .770 | 7.56 |

TABLE VI
Determination of Pore Radius
Method based on Poiseuille's Formulation

| Period | Experiment I | | | Experiment II | | | Experiment III | | |
|---------|----------------|-------|-----------------|----------------|-------|-----------------|----------------|-------|-----------------|
| | t hrs. | Q | $R \times 10^6$ | t hrs. | Q | $R \times 10^6$ | t hrs. | Q | $R \times 10^6$ |
| 1st cc | 1 _a | 1.240 | 157.4 | 1 _a | 1.400 | 167 | 1 _a | 1.640 | 181 |
| 2nd cc | | .865 | 131.7 | | .988 | 141 | | 1.020 | 143 |
| 3rd cc | | .750 | 122.6 | | .646 | 114 | | .654 | 115 |
| 4th cc | | .678 | 116.6 | | .510 | 101 | | .480 | 98.1 |
| 5th cc | | .630 | 112.4 | | .410 | 90.6 | | .348 | 83.5 |
| 6th cc | | .571 | 107.0 | | .323 | 80.5 | | .282 | 75.2 |
| 7th cc | | .566 | 106.5 | | .266 | 73.0 | | .234 | 68.5 |
| 8th cc | | .520 | 102.1 | | .230 | 67.9 | | .207 | 64.4 |
| 9th cc | | .475 | 97.6 | | .210 | 64.9 | | .190 | 61.7 |
| 10th cc | | .462 | 96.2 | | .200 | 63.3 | | .178 | 59.7 |
| 11th cc | | | | | | | | .174 | 59.1 |
| 12th cc | | | | | | | | .172 | 58.7 |
| 1st | 1 | .461 | 96.1 | 1 | .198 | 63.0 | 1 | .172 | 58.7 |
| 2nd | 2 | .820 | 90.6 | 2 | .400 | 63.0 | 2 | .355 | 59.6 |
| 3rd | 3 | .970 | 80.5 | 3 | .600 | 63.0 | 3 | .527 | 59.3 |
| 4th | 5 | 1.785 | 84.6 | 5 | .995 | 63.0 | 5 | .865 | 58.9 |
| 5th | 1 | .352 | 84.0 | 1 | .180 | 60.0 | 7 | 1.220 | 59.1 |
| 6th | 2.5 | .810 | 80.6 | 2 | .350 | 60.0 | | | |
| 7th | 3 | .960 | 80.1 | 3 | .535 | 60.0 | | | |
| 8th | 5 | 1.760 | 84.0 | 5 | .900 | 60.0 | | | |
| 9th | 7 | 2.065 | 76.9 | 7 | 1.250 | 60.0 | | | |
| 10th | 10 | 2.910 | 76.4 | | | | | | |

a. Volume Q calculated for a one hour interval.

In Table IV the values listed are those obtained after several hours, when the permeability has become practically constant. Tables V and VI, however, give the rate of flow from the moment the experiment was started and show the decrease of effective radius with time. If it is correct to assume that the decrease in permeability is caused by a partial clogging of the pores, it is entirely justifiable to plot the apparent radii against time and extrapolate this curve to zero time. In this way it should be possible to obtain the value for pore radius before any clogging of pores has occurred, and these values should be comparable with those obtained by the capillary rise method, since in the latter method liquid is allowed to come in contact with

a fresh and unaltered pore surface. A comparison between the observed values for the capillary rise method and the observed and extrapolated values for Poiseuille's method is given in Table VII.

TABLE VII
Comparison of Pore Radius determined by Two Independent Methods

| Solid | Pressure packing in pounds | Liquid | Pore Radius $\times 10^6$ | | |
|------------------------|----------------------------|------------|---------------------------|------------------------------|--------------|
| | | | Capillary Method | Poiseuille's method Observed | Extrapolated |
| Carbon | 2500 | Benzene | 9.29 | | |
| | | Chloroform | 9.36 | | |
| | | Toluene | 9.26 | | |
| | | Water | | 8.90 | 9.20 |
| | | | | 8.79 | 9.12 |
| | | 8.80 | 9.30 | | |
| | | 8.85 | 9.32 | | |
| | | — | — | — | |
| Average Carbon | | | 9.30 | 8.83 | 9.23 |
| Carbon | 1500 | | | 11.89 | |
| | | | | 11.82 | |
| | | | | 11.59 | |
| | | | | — | — |
| Average SiO_2 | | | | 11.77 | |
| SiO_2 | 3000 | Water | 210.6 | | |
| | | Benzene | 210 | | |
| | | Water | | 157.4 | 193 |
| | | | | 167 | 203 |
| | | 181 | 220 | | |
| | | — | — | — | |
| Average | | | 210.3 | 168 | 205 |

It seems hardly necessary to remark that this agreement is astonishingly close; for carbon black packed under 2500 pounds pressure, a radius of 9.30×10^{-6} centimeters by the one method as compared with 9.23×10^{-6} centimeters by the other, and for silica packed under 3000 pounds pressure, 2.10×10^{-4} centimeters, as compared with 2.05×10^{-4} centimeters. We feel convinced that both these methods are fundamentally correct and that if the conditions described in the first portion of this article are observed, both methods should give strictly comparable and closely checking results for both collodion membranes and membranes composed of compressed powdered solid. In fact, it should be less difficult to obtain close checks with collodion and similar membranes since in them the pores would tend to be more uniform in shape and in size. We believe, moreover, that this work may well serve as an answer to the criticisms which Gurohot directed against the use

of Poiseuille's formulation for permeability measurements, and which Hitchcock expressed in regard to the use by Bartell and Carpenter of Jurin's law for pore radius measurements.

Some few additional miscellaneous observations on the properties of these membranes might be of interest. The following brief table gives the number of pores per square cm. of membrane surface calculated from the permeability data of Bartell and Carpenter,¹ the number for the largest and smallest pores of membranes reported by Hitchcock² in his original paper, and the number for the carbon black and silica membranes employed by us and calculated from the values for the permeability and pore radius.

TABLE VIII
Comparison between Pore Radius and Number of Pores

| Observer | Type of Membrane | $R \times 10^6$ | Number of pores per sq. cm. | |
|-----------------------|------------------|--------------------|-----------------------------|--------------------|
| Bartell and Carpenter | Collodion | 84.0 | 13.4×10^3 | |
| | | 46.7 | 18.3×10^3 | |
| | | 35.0 | 15.6×10^3 | |
| Hitchcock | Collodion | 2.08 | 7×10^{10} | |
| | | .27 | 270×10^{10} | |
| Bartell and Osterhof | Carbon Black | 11.89 | 9×10^8 | |
| | | 1500 lbs. pressure | 8.90 | 14.6×10^8 |
| | | 2500 lbs. pressure | 7.46 | 20.8×10^8 |
| | Silica | 181.0 | 3.26×10^6 | |
| | | 3000 lbs. pressure | 58.7 | 30.9×10^6 |

It is noticeable in the case of the carbon black, and more markedly so in that of the silica membranes that as the mean effective pore radius decreases the number of pores in unit cross-section increases. On the assumption that a mechanical clogging of the larger pores occurs the increased number may be explained in two ways. One large pore may form several smaller ones, or the measureable effect of smaller pores which were present from the start may become more noticeable. In the silica membranes we have an extreme case in which the apparent number of pores has increased tenfold.

From a knowledge of the number of pores in the cross-section of the membrane and the rate of flow of liquid through it we can calculate the mean velocity in centimeters per second of the liquid in a given pore. This has the value of 9.11×10^{-2} cm. per second for Carpenter's least permeable membrane; for carbon packed under 2500 lbs. pressure the value is $4.08 \times$

¹ Bartell and Carpenter: *J. Phys. Chem.*, 27, 252 (1923).

² Hitchcock: *J. Gen. Physiol.*, 9, 759 (1926).

10^{-4} cm. per second. According to Reynolds' formula for the critical velocity at which turbulent flow commences, $V = \frac{1000 \eta}{d R}$, the critical velocity in the

first case would be more than 10^5 cm. per second, and in the latter case around 10^6 cm. per second. The difference between the actual velocity and the calculated critical velocity is so great that irregularities in the direction or shape of the pores would scarcely be expected to cause turbulent flow.

Hitchcock, (*loc. cit.*) by the application of Poiseuille's law, calculated that the pore radius of his collodion membranes varied from 3×10^{-7} to 20×10^{-7} cm. As was stated, the lower values are of doubtful significance since they cover a range of only five to ten molecular diameters and it is far from certain that the apparent viscosity of the liquid in such narrow pores is the same as it would be *en masse*. In attempts to apply the method of Bartell and Carpenter to the membranes used, he reported lack of success even with the use of much greater pressures (their pressures ranged from 1.76 to 4.23 kg. per sq. cm.) It is quite possible, however, that he did not employ pressures sufficiently great since for his membrane, B 15, with a radius of 2.08×10^{-6} the necessary pressure is 70.65 kg. per sq. cm. while for B 20 with a radius of 0.99×10^{-6} the pressure is 148.5 kg. per sq. cm. Naturally in cases such as this it would be more advantageous to employ a method based on Poiseuille's law.

Summary

The applicability of methods based on Poiseuille's law and on the capillary rise formulation for the determination of membrane pore radii has been discussed. Various sources of error which might invalidate their use have been considered and the conditions have been stated under which these methods should give accurate results. Experimental work with membranes formed by compression of finely powdered carbon and silica has shown that if these conditions are satisfied both methods give comparable and closely checking results. Aside from questions of experimental convenience in certain specific cases, there is, so far as we can see, no reason to prefer one method over the other.

In the determination of adhesion tension of solid against liquid by the pressure displacement method, in which displacement cells are employed, it is necessary to know the pore radius existing between the compressed particles of solid. The most convenient method for this determination is the capillary rise (*i.e.* pressure) method. The data presented in this paper appears to be sufficient to justify the use of that method.

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157A-1208

SOME EXPERIMENTS ON IRON

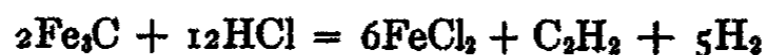
BY LAWRENCE GANE KNOWLTON

Introduction

As the title indicates, this investigation has to do with various experiments involving iron. The first three parts of the work deal with new methods for the determination of carbon in iron. The study of the tin-iron alloys was taken up with the object of determining the form of carbon when dissolved in iron. The next division is concerned with the effect of aniline on the rate of solution of iron in acid with the result that it can be classed with a group of compounds which act similarly. Next, some work on the reduction of nitrobenzene which was undertaken originally, to determine the difference in amount of corrosion of iron in sodium sulfate and sodium chloride solutions, but which eventually led to other results. Lastly, some experiments on passivity which were carried out with tin, but could be duplicated with iron in appropriate concentration of nitric acid.

An Electrolytic Method for Total Carbon

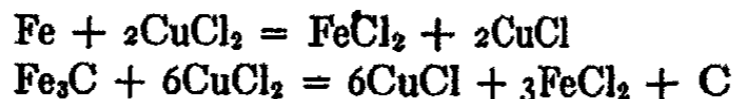
When iron dissolves in hydrochloric or sulfuric acids, much of the combined carbon, in the form of iron carbide, reacts with the acid forming hydrocarbons and leaves a small amount of carbon behind. This is due to the presence of nascent hydrogen at the point where the iron carbide is reacting. Under these conditions the carbon readily combines with the hydrogen. A possible reaction would be as follows:



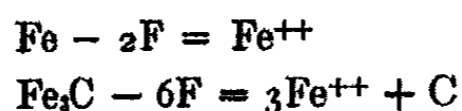
A small amount of the carbon of the iron carbide does not unite with the hydrogen of the acid which accounts for the carbon remaining. That the combined carbon is not reduced to hydrocarbons by nascent hydrogen, was proved by making a piece of iron, high in carbide, cathode in a sodium sulfate solution. No trace of hydrocarbons was found in the hydrogen evolved.

If iron is dissolved in nitric acid, sp. gr. 1.2, the concentration used in the determination of graphitic carbon, most of the combined carbon is oxidized to soluble compounds which color the solution brown; a little carbon dioxide and a trace of hydrocarbons are formed. Only graphitic carbon remains behind after the iron dissolves.

If it is desired to dissolve the iron sample and have all the carbon remain, as in the determination of total carbon, the potassium copper chloride method may be used. The sample is dissolved in a solution containing the potassium copper chloride and some hydrochloric acid. The concentration of the acid is not high enough to react with the iron carbide. The reactions involved are as follows:



Iron made anode in a solution of certain electrolytes should dissolve and leave all its carbon behind as the hydrogen is given off at the cathode and thus has no opportunity to react with the carbon of the iron carbide, as it is broken down. This method is similar to the potassium copper chloride method except that a different method of solution of the iron is used. The electrochemical equations involved are as follows:



Justum¹ employed this method for determining total carbon. He made a steel rod anode in a dilute hydrochloric acid solution, sp. gr. 1.1, using a platinum cathode. The current was allowed to run over night, 10 or 15 grams of steel being dissolved. The carbon could then be filtered off and determined by combustion in the usual manner. No figures are given as to the accuracy of his results. It would seem, however, that the iron would not dissolve uniformly thus giving cause for error.

The method used in these experiments was to place the iron turnings in a platinum dish and make this anode. A strip of copper served as cathode. The current from two storage batteries was used which gives 3.6 volts and .65 amperes at the start. The amperage changes considerably during the run. As electrolyte, a 10% solution of sodium chloride was first employed. It was found that chlorine was evolved which of course would not be expected as the potential required to make iron dissolve, is less than that to discharge chlorine. To find out the cause of this, some current-voltage readings were taken. It was found that after the current starts, the amount flowing through the circuit gradually decreases. This is explained as due to the increased resistance caused by the iron hydroxide formed. This would form around the iron and increase the resistance between the platinum dish and the iron. If acid is added, or the solution is stirred, the current goes up again. When the iron hydroxide forms around the iron it becomes easier to discharge the chlorine than to force the iron to dissolve.

A 10% solution of sodium sulfate was substituted for the sodium chloride and while some oxygen was evolved it does not oxidize the carbon as can be seen from the results.

About 1.5 grams of iron turnings were weighed out and placed in the platinum dish. The sodium sulfate solution was then poured in, and the current started. As mentioned before, as the electrolysis proceeds, iron hydroxide appears and settles down on the turnings tending to prevent the dissolving of the iron. Acid could be added but there is danger of adding enough to attack the iron. Instead, the solution containing the iron hydroxide is poured off leaving the undissolved iron behind in the dish. More sodium sulfate solution was added and the electrolysis continued. This process has to be repeated several times. A half day or more is required for all the iron to dissolve. The contents of the platinum dish is then added

¹ Chem. News, 41, 17 (1880).

to that already poured off and the mixture warmed with 15 or 20 cc. of concentrated hydrochloric acid to dissolve the iron hydroxide. The carbon is then filtered off on a Gooch crucible and determined by combustion in the usual way.

The results check very closely with those found by the ordinary method of combustion of the iron sample. A white iron sample was first tried, which contains all the carbon in the combined form, so that if any of the carbon were removed in the form of a gas, it would be noticeable in the results. The other two are gray iron, number three being one analyzed by the U. S. Bureau of Standards.

| | 1 | 2 | 3 |
|---------------------|-------|-------|-------|
| Ordinary Combustion | 2.13% | 3.00% | 2.19% |
| Electrolytic Method | 2.18% | 3.00% | 2.27% |

Different determinations on the same sample checked closely. In the case of No. 1, 2.15, 2.18 and 2.22 were the results obtained.

This method is accurate and would be satisfactory where rapid determinations are not required.

An Electrolytic Method for Graphitic Carbon in Iron

Haber¹ states that an iron cathode corrodes in an ammoniacal solution of ammonium nitrate. Here, as the iron carbide dissolves, it would come in contact with nascent hydrogen from the electrolysis and form hydrocarbons. Thus there would be only graphitic carbon left after the solution of the iron.

A piece of sheet iron was made cathode in a strong solution of ammoniacal ammonium nitrate and the current density kept low as recommended in the above article. The iron did corrode very slowly but it was found that a piece of iron in a similar solution corroded about as much without the use of current. Heating the solution or increasing the current, does not increase the rate of corrosion appreciably. No determinations of the amount of carbon remaining were made as it would take an extremely long time for all the iron to dissolve. The current has nothing to do with the corrosion process. A spot of iron or iron carbide dissolves as anode in a local cell and at another point, the cathode, hydrogen is set free. Under these conditions the iron carbide does not come in contact with nascent hydrogen as it is broken down, so no hydrocarbons will be formed. Then, if the iron dissolved completely, most or perhaps all of the carbon should be left behind. When the iron dissolves in either hydrochloric or sulfuric acids, as mentioned before, the carbon does come in contact with the nascent hydrogen and forms the hydrocarbons which are evolved.

If the iron should dissolve as cathode, the hydrogen given off at the same time should react with the combined carbon and only graphitic carbon should remain behind. There is, however, the possibility of the hydrogen

¹ Z. Elektrochemie, 7, 733 (1901).

reducing the nitrate radical rather than reacting with the combined carbon, and if this were the case, more than the graphitic carbon should remain behind.

Effect of Depolarizing Agents on the Amount of Carbon remaining when Iron dissolves in Acid

As stated before, when iron dissolves in hydrochloric or sulfuric acids, the iron carbide reacts with the acid forming hydrocarbons which pass off as a gas. If a depolarizer were present the hydrogen from the above reaction might be oxidized and thus not have an opportunity to react with the carbon of the iron carbide. This would leave more than the usual amount of carbon behind. There is also a possibility that the depolarizer may be able to oxidize the carbon formed, either graphitic or carbide. The effect of the depolarizer may be tested by the amount of carbon remaining after the iron has dissolved.

The idea for this work came from the fact that the iron-tin alloy mentioned later, left more carbon behind when dissolved in aqua regia, than in nitric acid of the concentration used for determining graphitic carbon. This effect will be taken up later.

Potassium permanganate was chosen as the depolarizer for these experiments. A standard solution, rather concentrated, from .05 to .06 grams per cc., was used. This was boiled to remove organic matter and filtered through an asbestos filter which removes manganese dioxide. Samples of the iron turnings, always within .01 grams of 1.55 grams, were placed in a beaker and a definite volume of the standard permanganate solution added from a burette. The total volume was made up to 50 cc. by adding water. Four cc. of concentrated sulfuric acid were then added and the action usually allowed to proceed without heating. After the first vigorous reaction, the beaker is heated and more sulfuric acid added to be sure that all the iron carbide has dissolved. Iron carbide dissolves less readily than iron. Mellor states that N/10 hydrochloric acts on it at 80°, and the N acid gradually dissolves it at ordinary temperatures.

A series of runs was made using two different iron samples. No. I is white iron with a total carbon content of 2.13% and no graphitic carbon. No. II is a gray iron, total carbon 3.31%, and graphitic carbon 2.54%. The results obtained are as follows:

| Gr. KMnO ₄ | I | | II | |
|-----------------------|----------|----------|-----------------------|----------|
| | cc. acid | % Carbon | Gr. KMnO ₄ | % Carbon |
| 1—none | 4 | .75 | 1.3 | 3.01 |
| 2—none | 8 | .55 | 1.5 | 3.08 |
| 3—1.5 | 4 | 1.9 | 1.7 | 3.16 |
| 4—1.8 | 4 | 2.12 | 2. | 3.11 |
| 5—2.1 | 4 | 2.14 | 2.2 | 3.13 |
| 6—2.3 | 4 | 2.13 | 2.4 | 3.02 |
| 7—2.7 | 4 | 1.64 | 2.5 | 2.98 |
| 8—2.95 | 4 | 1.25 | | |
| 9—2.3 (in 75 cc.) | 5 | 2.04 | | |
| 10—2.3 | 7 | 1.9 | | |

The first runs were made with white iron and, as can be noted, with the correct concentration of permanganate the total carbon can be obtained, which would suggest using this as a method for total carbon. The runs were then made with the gray iron with less satisfactory results. The maximum percentage of carbon is about .15% less than the total carbon. This was found to be due to the oxidation of the graphitic carbon by the permanganate, as will be explained later.

It will be seen from the results, that there is a maximum in the amount of carbon remaining which falls off on either side. This is explained as follows. With a smaller amount of permanganate present, it does not oxidize the hydrogen rapidly enough to prevent some of the hydrogen reacting with the carbon of the iron carbide. This carbon then escapes in the form of hydrocarbons. With too much permanganate present, it oxidizes the carbon.

Increasing the amount of acid (9) would be expected to decrease the amount of carbon as the iron would dissolve more rapidly, thus giving the permanganate less opportunity for its action on the hydrogen. Making the solution more dilute (8) would leave less permanganate in contact with the iron to act. This could be overcome by stirring.

As mentioned, the maximum amount of carbon that was left, was the same as the total carbon in the case of the white iron but somewhat less with gray iron. Another gray iron gave similar results whose total carbon was 2.19% and graphitic carbon 1.82%.

III

| Gr. KMnO_4 | % Carbon |
|---------------------|----------|
| 1.8 | 1.72 |
| 2.1 | 2.00 |

One would expect the white iron to give the lower results because of the larger amount of combined carbon which has an opportunity to go off as hydrocarbons. It was thought that by changing the conditions during the dissolving of the gray iron, the carbon remaining could be brought up to the total carbon content. The acid content was then reduced to 2 cc. of concentrated sulfuric acid. Under these conditions some iron salt is precipitated. This does not dissolve readily even when more sulfuric acid is added. Hydrochloric acid, however, will dissolve it. The amount of carbon remaining was not raised by this change. Other runs were made, stirring until the permanganate was used up. This did not change the results appreciably. Better results were obtained if the permanganate was added gradually and stirred during the addition. Gradual addition would tend to prevent the permanganate becoming concentrated enough to oxidize the carbon while stirring would keep the permanganate in contact with the iron, as it dissolved.

The explanation of the low results in the case of the gray iron was finally found to be due to the oxidation of the graphitic carbon. To determine whether the permanganate oxidizes the graphitic carbon, the following experiment was carried out. Gray iron, II, was dissolved in nitric acid, sp. gr. 1.2, which leaves only graphitic carbon undissolved. This carbon was filtered

off on a Gooch crucible, then placed in a beaker with 50 cc. of a solution containing 4 cc. of concentrated sulfuric acid and .25 grams of permanganate. The solution was heated for 15 minutes at a temperature of 60° – 65°C. The graphitic carbon content had then dropped from 2.54% to 2.28%.

As mentioned before when iron dissolves, iron carbide goes into solution after the iron. In the case of the gray iron, with little combined carbon, the graphite will come out at the first part of the action and thus is exposed to the oxidizing action of the permanganate for a considerable length of time, while the concentration of the permanganate is still high. With white iron the carbon does not come out until the last of the action and is in contact with a more dilute permanganate for a shorter length of time. Thus there is little opportunity for its oxidation.

It would then be logical to conclude that the permanganate could be added some time after the acid had begun to act on the iron and be more effective than if added before the action starts. This conclusion was borne out by experiments. The acid was allowed to act for a certain length of time, five to seven minutes, and then the permanganate was dropped in rapidly, about as fast as it was used up. The addition of the permanganate was continued until the action of the acid on the iron was practically complete. With iron II, this method gave a value of 3.24%, .07% less than the total carbon value. With iron III, it gave 2.17%, .02% less than the total carbon and almost within the limit of experimental error. Here are two causes of the lower results in the case of iron II. First; it has a higher total carbon content thus there is more likelihood of the carbon being oxidized. Second; the turnings are not uniform as is the case with iron III. Some of the smaller particles of iron would dissolve completely before the permanganate is added, thus losing the combined carbon as hydrocarbons.

From the above, it is evident that the method given would be practical for the determination of total carbon in white iron, as it is accurate and as rapid as any method involving the solution of iron previous to combustion. It would not be reliable in the case of the gray iron, due to the difficulties mentioned.

As mentioned before, if iron is dissolved in aqua regia it leaves more than the graphitic carbon. Runs were made using the same iron samples as before. The results follow:

| No. of cc.HNO ₃ | No. of cc.HCl | No. of cc.H ₂ O | Iron sample used | % Carbon |
|-------------------------------|------------------|-------------------------------|---------------------|----------|
| 8 | 21 | 15 | White I | .89 |
| 0 | 25 | 25 | White I | .32 |
| 8 | 24 | 0 | Gray II | 2.87 |
| 8 | 0 | 24 | Gray II | 2.56 |

These results show that more carbon remains when aqua regia is used to dissolve the iron than if either acid were used alone. This would be explained as follows. When there is a mixture of the two acids present, the nitric acid or the chlorine produced would oxidize the hydrogen preventing

the formation of hydrocarbons. Of course nitric acid alone would be capable of oxidizing this hydrogen. There is an added effect, however; some of the nitric acid is used up in oxidizing the hydrochloric acid thus preventing it from acting on the carbon. This would cause more carbon to be left behind.

Some runs were also made to determine the oxidizing effect of hot aqua regia and chlorine on the carbon from the white iron and the graphitic carbon from the gray iron. The carbon from the white iron was produced by treatment with permanganate and acid. The graphitic carbon was produced in the usual manner. The results follow:

| cc. of HCl | cc. of HNO ₃ | cc. of water | Source of Carbon | Before | After |
|------------|-------------------------|--------------|------------------|--------|-------|
| 24 | 8 | 15 | White iron I | 2.13% | 1.36% |
| 24 | 8 | 15 | Gray iron III | 1.8% | 1.8% |
| 24 | 8 | 0 | Gray iron III | 1.8% | 1.8% |

When chlorine was bubbled into heated water containing the carbon from the white iron, the carbon content went down to 1.28%. Using the graphitic carbon from iron III, after similar treatment with chlorine for an hour and a half, there was no loss in carbon. Aqua regia and chlorine are similar in that they oxidize the carbide carbon but not the graphitic carbon.

It would follow, then, that if chlorine were bubbled into an acid solution in which iron was dissolving, it should raise the amount of carbon as was the case with permanganate. Of course the experiment should be so regulated as to prevent the oxidation of the carbide carbon as much as possible.

Runs were made with both white and gray iron. The iron turnings were placed in the acid and heated to 60° – 80°. Chlorine was bubbled in from a cylinder as long as there was any action.

| cc. of HCl | cc. of water | Iron sample | % Carbon |
|------------|--------------|-------------|----------|
| 10 | 40 | II | 2.94 |
| 30 | 20 | I | 1.00 |

The results do not reach the value for total carbon in either case due either to the escape of hydrocarbons or to the oxidation of some of the carbide carbon. It would probably be possible, by regulating conditions, to bring these values up to some extent. However, it would be more difficult to regulate the concentration of the chlorine than that of the permanganate. The rate of solution of the iron could be readily controlled by the concentration of the acid and the temperature.

Effect of Tin on Carbon in Iron

In Percy's Metallurgy,¹ Eyferth has experimented on the action of tin on cast iron. He thought that if 25% tin was added to and stirred with molten gray cast iron, the whole of the graphitic carbon would separate out and this would be left behind in the crucible when the alloy is poured out. If this were true it ought to have an interesting bearing upon the form of carbon

¹"Metallurgy: Iron and Steel", 163 (1864).

in the melt. If there is a reversible equilibrium between combined and uncombined carbon in the melt, then tin should displace all the carbon from the melt or if we assume with Jeffries and Archer that there is no combined carbon in the melt, it should also displace all the carbon.

The iron-tin system was first worked out by Isaac and Tammann.¹ Iron and tin are not miscible in all proportions in the melt: between 50% and 89%, two layers are formed in equilibrium at 1140°C. Below this temperature mixed crystals of 19% tin content deposit from the iron rich layer leaving the melt containing 89% tin. At 893°C a reaction occurs between the iron rich mixed crystals and the tin rich melt with the formation of a compound whose formula is not given. The system was further investigated by Wever and Reinecken.² The diagram of the system was changed somewhat and the composition of the iron-tin compounds separating out was determined.

An article on the iron-tin-carbon system by Goerens and Ellingen,³ has been published. The diagram is not worked out but the constituents of the system are determined by cooling curves and microscopic examination. The miscibility gap between iron and tin in the melt is increased by the presence of carbon. The solid phases separating out from the iron layer are said to be first, austenite containing tin, then cementite, the iron-tin compound and lastly a ternary eutectic. Analysis of the iron layer is made for tin, total and graphitic carbon. No mention is made of whether carbon is thrown out or not.

To verify Eyferth's experiments, various alloys of iron and tin were made up by melting gray iron in the induction furnace and adding tin. The resulting melt was poured into sand. Graphitic carbon was thrown out but by no means the whole amount, as shown by the following table:

| | Tin | T. C. | G. C. |
|---------------------|---------------------------|---------------------------|-------------------|
| Iron for Alloy 1 | | 2.99 | 2.95 |
| Alloy 1 | 12.8 | 2.19 | .3 |
| Iron for Alloys 2-6 | | 3.31 | 2.54 |
| Alloy 2 | 15 | 2.1 | .06 |
| Alloy 2 annealed | 15 | 2.1 | .29 |
| Alloy 3 | 15 | 2.3 | .22 |
| Alloy 4 | 7.5 | 3.00 | 1.75 |
| Alloy 5 | 13 | 2.6 | .34 |
| Alloy 6 | 16 | 2.2 | .26 |
| | T. C. on basis of iron | G. C. on basis of iron | Loss of carbon |
| Alloy 1 | 2.52 | .35 | .5 |
| Alloy 2 | 2.48 | .07 | .8 |
| Alloy 2 annealed | 2.48 | .34 | .8 |
| Alloy 3 | 2.7 | .26 | .6 |
| Alloy 4 | 3.2 | 1.9 | .1 |
| Alloy 5 | 3.00 | .39 | .3 |
| Alloy 6 | 2.64 | .31 | .7 |

¹ Z. anorg. Chem., 53, 281 (1901).

² Z. anorg. Chem., 151, 349 (1926).

³ Metallurgie, 7, 72 (1910).

From the above results it will be seen that .8% is the most carbon thrown out which amounts to only about a third of the graphitic carbon contained in the original iron. The amount of carbon thrown out of the alloy as graphite, increases as the tin content of the alloy is increased; alloy 4 with 7.5% tin lost very little while alloys around 15% tin lost .6-.8%. The graphitic carbon content of the alloy also decreases with increase in amount of tin as a comparison of alloy 4 with the others shows. The tin content of the iron can only be increased to a certain point, 16%, after which two layers appear, the tin-rich layer containing about 90% tin. This tin-rich layer contains no carbon. The amount of carbon in the iron layer can not be lowered beyond a certain amount when the iron layer is saturated with tin. The amount of carbon thrown out, however, increases with increasing amounts of tin as more iron would enter the tin layer and this iron would lose all its carbon. This would also effect the accuracy of the results on the basis of the iron present (columns 3 and 4). It would make the amount of carbon thrown out as graphite greater than it apparently is whenever a tin rich layer is formed.

As an analogy to this effect of tin in displacing carbon from iron, can be taken the effect of alcohol on a solution of sodium chloride. Sodium chloride is only slightly soluble in alcohol and if alcohol is added to a salt solution, the salt precipitates out, if enough alcohol is added all the salt should crystallize out. In like manner carbon is not soluble in tin and when tin is added to a solution of carbon in iron carbon comes out. If enough tin were present to dissolve all the iron, all the carbon should be thrown out.

It will be well to consider here what conclusions can be drawn, from this work and that of others, as to the form of carbon in the melt. There are three possibilities, two of which have already been mentioned. They are

1. It may be present as dissolved carbide.
2. It may be present as dissolved carbon.
3. There may be a reversible equilibrium between the two represented as follows $\text{Fe}_3\text{C} \rightleftharpoons 3\text{Fe} + \text{C}$.

At first thought it would seem possible to determine this from the form in which carbon separates from solution. This line of attack is not conclusive, due to the fact that the form in which a substance separates from solution is not necessarily the one in which it exists in solution. Any electrolyte dissolved in water gives numerous indications that it is present in the form of ions. However, when the solution is cooled, the substance itself, not its ions, comes out. Thus whether graphite alone, cementite alone, or sometimes one or the other separates, gives no evidence of the form of carbon in the melt.

Some authors base their opinion as to this point on such evidence. Desch,¹ does not commit himself but indicates that he considers the reversible equilibrium in solution possible to explain the separation of graphite and cementite.

Hatfield² has carried out a number of experiments with different iron samples including those containing silicon, in which graphite is generally

¹ "Metallography," 368 (1913).

² Proc. Roy. Soc., 85A, 1 (1911).

considered to be the form that separates from solution. Microscopic evidence shows that, in the cases studied, carbide must separate out from solution before carbon can appear and only this structurally free carbide can dissociate. Annealing carbon is formed by the decomposition of the free carbide from which it is produced. That is, there must be an intermediate formation of cementite before free carbon can be produced. It would be interesting to see if the same results could be obtained with a higher silicon iron than the ones used or also with a high carbon content alone. Here it is more likely that carbon separates from solution. Hatfield does not mention in this article whether he believes his experiments prove the presence of iron carbide in solid solution but this is indicated in his discussion of an article by E. D. Campbell.¹ This, as has been shown, would not be necessary as the iron carbide could form as it separated out.

Sauveur² states that many evidences point to carbon being dissolved in molten iron as carbide. At this point no statement is made as to what these evidences are. However,³ a diagram is given for the solubility of carbon in molten iron which has some bearing on the subject. At 1823°C and 6.67% carbon there is a slight break in the curve and the melt is said to be liquid Fe₃C. Again at 2220°C and 9.6% carbon liquid Fe₂C is said to be present. At this temperature there is another break and above this the Fe₂C decomposes into iron and graphite as the solubility becomes less. The latter then separates from solution. There is no evidence to show that these compounds are not decomposed in the melt, even if they should separate as the iron cooled. Also, there is considerable disagreement as to this part of the iron-carbon diagram. Tammann⁴ refers to another diagram which has no breaks at the points mentioned and shows no decrease in solubility of carbon above 2200°C.

Sauveur⁵ also states that if carbon alone is dissolved in solid iron it should collect in particles large enough to be visible under the microscope. This is not necessary, solutes never segregate in a definite portion of a liquid solution.

The separation of "kish", graphite on the surface of molten iron, also gives no proof of the form of carbon in solution. It might either form by separation from the melt directly, or by rapid decomposition of the iron carbide after this had come out.^{6,7}

Hoyt⁸ gives a summary of some work by E. D. Campbell. This has to do with the form of carbon in solid steel. A series of iron carbides of the general formula C_nFe_{3n} is thought to exist in steel. Their presence is indicated by the different hydrocarbons evolved when the steel is treated with hydro-

¹ J. Iron and Steel Inst., 2, 12 (1914).

² "The Metallography and Heat Treatment of Iron and Steel", 425 (1926).

³ Sauveur: "Metallography", 360.

⁴ Tammann: "Metallography", 235 (1925).

⁵ Sauveur: "Metallography", 394.

⁶ Hoyt: "Metallography", Part II, 143 (1921).

⁷ Sauveur: "Metallography", 430.

⁸ Hoyt: "Metallography", 186.

chloric acid and also from the color of the nitro derivatives formed when steel is dissolved in nitric acid. As the temperature increases the carbides in solid solution dissociate into others of lower molecular weight. The carbides also undergo what is termed ionoid dissociation into carbon and iron, with rising temperature. The hardness and other properties of steels are explained as due to the amount and condition of the different carbides present. The suggestion is made that austenite is a solid solution in which the carbides have undergone almost complete dissociation. This is based on the softness and electrical resistance of the austenitic iron. Campbell's work is thorough and he meets possible objections to his theory in a satisfactory way. He is dealing with carbon in solid solution, but if the carbides are completely dissociated in austenite they probably would be in the melt.

Jeffries and Archer¹ believe that only dissolved carbon is present in solution because the iron carbide molecules would be too large to diffuse. "When an intermetallic compound forms and dissolves in one of the component metals it is commonly considered to go into solution as such. For example, carbon is generally held to be in solution in gamma iron as cementite rather than as elementary carbon."

"From evidence available and particularly from a consideration of the phenomena of diffusion, the authors have reached the conclusion that this is not the case, but that the carbon in austenite is present as individual atoms of carbon. These atoms are undoubtedly held strongly to the neighboring iron atoms, but the union is not permanent. Diffusion must consist in a migration of carbon atoms, and not of groups or molecules containing several iron atoms. Such groups could not, on account of their size diffuse through the solid iron."

"According to this view, cementite has no existence except as a crystalline substance which not merely precipitates but is formed on the decomposition of austenite."

Going back to non-metallic solutions there are numerous examples of compounds having large molecules which are soluble and diffuse readily. Sugar and many other compounds can be brought forward to disprove the view of Jeffries and Archer.

The effect of tin in throwing out carbon from molten gray cast iron remains as evidence as to the form of carbon in solution. It is evident that, at the temperature at which the alloys are formed, only a certain amount of the tin will dissolve in the iron, after which two layers are formed. This is shown by the fact that increasing the tin content beyond a certain amount does not increase the amount of carbon thrown out of the iron layer. The carbon coming out of the molten iron indicates the presence of some free carbon. It might be assumed that the tin could react with the iron carbide forming an iron-tin compound and setting free carbon. This is not possible because the tin would react more readily with the free iron and even if the reaction did occur the iron would react with the carbon again.

¹ "The Science of Metals", 407 (1924).

The action of the tin, then, eliminates the possibility of the carbon being present as iron carbide alone. However, the results can be equally well explained from either of the other points of view. If there is a reversible equilibrium, $\text{Fe}_3\text{C} \rightleftharpoons 3\text{Fe} + \text{C}$ the tin can displace any amount of carbon as long as the concentration of the tin in the iron can be increased, because the equilibrium shifts to the right as the carbon is thrown out of solution. The fact that all the carbon is displaced from the iron in the tin layer, can also be explained by the shifting of the equilibrium to the right.

Thus there is no definite evidence to prove whether the carbon is present in the melt as such, or whether there is a reversible equilibrium between it and iron carbide.

To return to some properties of the alloy. From the carbon analyses given, it is evident that the alloys produced have a much higher combined carbon content than the iron which is used to make the alloy. This is not due to rate of cooling as an iron sample melted and cooled under the same conditions as the alloy undergoes no change in the amount of combined carbon. This combined carbon of the alloys is quite stable, as alloy 2 when heated over night at about 900°C showed an increase of only about .25% in graphitic carbon. The alloys made by Goerens and Ellingen have a high combined carbon content as the following table, taken from the article, shows:

| Sn added | Sn found | T. C. | G. C. |
|----------|----------|-------|-------|
| 7 | 4.89 | 3.32 | .24 |
| 9 | 6.64 | 3.11 | 1.11 |
| 12 | 9.09 | 3.32 | .52 |
| 15 | 8. | 3.2 | .72 |
| 15 | 8.92 | 3.17 | |
| 16 | 6.78 | 3.5 | .48 |
| 19 | 9.24 | 2.71 | .49 |
| 22 | 10.5 | 2.8 | .08 |
| 30 | 11.1 | 2.73 | .71 |

The tin then has the ability to raise the combined carbon content. It would seem logical to believe that the tin has some effect on the silicon in the iron. A white iron can readily be cast if the silicon content is low, but when the silicon content rises to 1%-2%, a gray iron will generally be produced. The gray iron used had a silicon content of 2.21%, enough to make it evident that the tin had some effect on the silicon in the iron of the alloy.

This action of silicon is believed to be due to its effect on the iron carbide, promoting its dissociation into iron and carbon. According to Hoyt¹, "The mode of occurrence of silicon in the silicon cast irons is still a matter of conjecture but it seems reasonable to assume that the silicon distributes itself between austenite and cementite, and that the silicon in the cementite makes

¹ "Metallography", 290.

that constituent break down more easily at high temperatures." Hoyt refers to Stead and Hatfield for this statement.

Stead¹ states that a carbosilicide crystallizes with iron carbide. What the composition of this carbosilicide is is not mentioned but it probably consists of mixed crystals of iron silicide and iron carbide, as mentioned by Gontermann in a reference given later. The diffusion of the silicide leads to the decomposition of the iron carbide. Silicide of iron when heated with pure silicon free white iron, decomposes the carbide in the white iron.

Hatfield² has analyzed and found silicon to be present with iron carbide. When manganese and sulfur, elements which promote the stability of cementite, are present less silicon is found with the carbide.

Gontermann³ has investigated the iron-carbon-silicon system. From an iron whose carbon and silicon content corresponds to the iron used for the above experiments, saturated silicon martensite separates out as primary crystals and solidification is concluded by a secondary crystallization of a mixture of saturated martensite and silicon cementite. He is evidently using the term martensite for austenite. The silicon cementite consists of mixed crystals of FeSi and Fe₃C.

It is evident, then, that silicon is present with cementite in the iron. None of the above authors make an attempt to explain how the presence of silicon makes the cementite break down into iron and graphite. In the case that Stead mentioned of the decomposition of silicon free white iron by heating with iron silicide, the silicon would have to diffuse into the cementite in order to make it decompose. That is, silicon is soluble in cementite. If the presence of silicon makes carbon less soluble in iron, the action of the silicon could be explained by saying that it dissolves in the iron, throwing out carbon. Then when iron containing silicon is cooled rapidly, the silicon simply crystallizes with the cementite, but if allowed to cool slowly or reheated to around 1000°C the silicon diffuses into the cementite causing graphite to separate out and giving a gray color to the iron. Silicon does decrease the solubility of carbon in iron, for when 50% ferro-silicon is dissolved in molten iron a considerable quantity of graphite is thrown out.⁴ It is also possible that the silicon that is in solid solution, austenite, would lower the solubility of the carbon, and graphite would separate directly from this without undergoing the intermediate formation of cementite.

When the action of silicon is explained as above, it would seem that tin should act the same way, as it makes carbon less soluble in the liquid state. However, tin is not soluble in cementite,⁵ and cementite in itself is quite stable.⁶ "Nearly pure iron-carbon alloys do not graphitize readily."

¹ Engineering, 90, 508 (1910).

² Proc. Roy. Soc., 85A, 1 (1911).

³ Z. anorg. Chem., 59, 373 (1908).

⁴ Hague and Turner: J. Iron and Steel Inst., 2, 100 (1910).

⁵ Desch: "Metallography", 382.

⁶ Jeffries and Archer: "The Science of Metals", 314.

Tamaru¹ has investigated the tin-silicon system. The two metals are miscible in all proportions in the melt and silicon separates when the melt is cooled. No compounds or solid solutions are formed.

With this in mind it was thought that the tin of the alloy was dissolving the silicon, thus preventing its action on the cementite. To prove this, an alloy was made up to which enough tin was added to insure the formation of a tin layer. This tin layer contained no silicon but the iron layer showed a loss of about .3% silicon. The silicon had probably been thrown out as the alloy cooled. This was verified when silicon was found to be present mixed with the graphite thrown out. Eyferth also mentions that silicon was thrown out from his alloys. One would expect the silicon, as it was soluble in molten tin, to crystallize in the tin layer as it cooled. What has happened is that the silicon separates from the liquid solution because of the difference in density and the probable low viscosity of the molten tin. This is similar to the separation of "kish", graphite on the surface of the molten metal, when a high carbon iron is cooled. Also as no eutectic mixture of tin and silicon is formed, the tin layer remains liquid until its solidification temperature is reached, thus making it easier for the silicon to separate. In the iron layer the iron will solidify first so that the silicon when it crystallizes cannot separate out of the body of the alloy.

The tin of the iron layer, as it solidifies last, would hold the silicon in solution until after the cementite had crystallized. The pure cementite would then decompose less readily. This gives rise to a high combined carbon content.

The alloy produced is hard and brittle. The brittleness was evident when it was found that the alloy could be readily pounded up to a powder. The alloy could not be turned in a lathe even using stellite as a tool. However, it is not so hard as this would indicate. It will not scratch glass unless heated and quenched. Its effect in the lathe is probably due to a hard constituent in the alloy, possibly the iron-tin compound, which ruins the cutting edge of the tool. Similar cases are known in which it is impossible to turn soft metals which contain some hard constituent. In the spheroidizing process, steel which has been cooled rapidly, so that the cementite comes out in the form of spines or network, is annealed. During the process the cementite changes to globules or spheroids which makes the steel much easier to machine.

Effect of Aniline on the Rate of Solution of Iron in Acid

It has been stated that in the pickling of iron and steel, acid containing aniline removes the mill scale and does not attack the iron to such a large extent as acid alone. Other substances have been found which act similarly. A number of these substances are mentioned and their effect studied by A. Sieverts and P. Lueg.²

¹ Z. anorg. Chem., 61, 40 (1909).

² Z. anorg. Chem., 126, 193 (1923).

To test the action of aniline a strip of sheet iron, covered with a coating of mill scale, was placed in a 10% solution of sulfuric acid containing aniline. The acid was practically saturated with aniline and was kept at a temperature of 50°-60°. The mill scale is removed and much less hydrogen is evolved than if acid alone is used. Another experiment of a more exact nature was the following: A piece of iron was placed in a beaker of 10% sulfuric acid heated to 50°-60°. The hydrogen evolved was collected which amounted to 40 cc. Another piece of the same iron of the same dimensions was placed in 150 cc. of the 10% acid containing 10 cc.-15 cc. of aniline. This was heated at the same temperature and for the same length of time as the other. Only about 5 cc. were evolved in this case.

The action of aniline and other substances in cutting down the hydrogen evolution may be due to:

1. The formation of a film on the metal which would increase the resistance in the local cells on the iron. This would slow up the solution of the iron, as it is an electrolytic process.

2. Through the presence of this film or by some other phenomena, the overvoltage of the hydrogen becomes higher than in acid alone. This makes it more difficult for the iron to go into solution.

Some work has been done on the determination of film resistance by means of an oscillograph.¹

A rise in overvoltage could be determined by means of the usual current-voltage readings. The decomposition voltage would have a higher value if the overvoltage of hydrogen on iron was raised.

A simple potentiometer outfit was set up using a voltmeter to register voltage and a milliammeter for current. When electrolyzed, a sulfuric acid solution of aniline gives aniline black at the anode so that the current begins to flow almost immediately. To prevent this, the anode was placed inside a porous cup. If acid is used around the anode, which is platinum, it increases the tendency for the iron to dissolve so a solution of sodium hydroxide was substituted. 2N sulfuric acid is used around the cathode. The iron used was not attacked appreciably at this concentration. The current-voltage run was first made with acid alone around the cathode, then with acid containing aniline, practically saturated.

| Acid Alone | | Acid and Aniline | |
|------------------------|------------|-----------------------|------------|
| Volts | Milliamps. | Volts | Milliamps. |
| 0 | .1 | 0 | .1 |
| 1.25 | .1 | 1.25 | .1 |
| 1.3 | .1 | 1.3 | .1 |
| 1.35 (Decomp. voltage) | .5 | 1.35 | .1 |
| 1.4 | .9 | 1.4 (Decomp. voltage) | .4 |
| 1.5 | 1.8 | 1.45 | .7 |
| | | 1.55 | 1.00 |

¹ Bur. Standards Sci. Paper No. 504 (1925).

It will be seen that the decomposition voltage is about .05 of a volt higher when the aniline is present, due to the rise in the hydrogen overvoltage at the cathode.

Current-voltage runs were next made at the cathode using a calomel electrode.

| Acid alone | | Acid and Aniline | |
|------------|------------|------------------|------------|
| Volts | Milliamps. | Volts | Milliamps. |
| .48 | .5 | | |
| .5 | .7 | | |
| .525 | 1 | .58 | 1 |
| .58 | 2 | .625 | 2 |
| .615 | 3 | .66 | 3 |
| .625 | 4 | .68 | 4 |
| .645 | 5 | .70 | 5 |
| .66 | 6 | .72 | 6 |
| .675 | 7 | .725 | 7 |

When aniline is present, the voltage, for the same amount of current has risen considerably. This amounts to about .05 volt in each case, the same as the rise in the decomposition voltage, which gives conclusive evidence that the rise in overvoltage has occurred at the cathode.

Reduction of Nitrobenzene

When iron is placed in sodium chloride solution which would ordinarily contain dissolved oxygen from the air, it corrodes more readily than it would in water containing the same amount of dissolved oxygen. This is due to the type of film formed on the iron. In water alone, iron reacts producing hydrated iron oxide at the spot where it dissolves, which tends to cut down the rate of corrosion. In sodium chloride solution iron reacts producing first ferrous chloride which then diffuses and forms hydrated iron oxide at the point where it meets the sodium hydroxide coming from the cathodic area. This leaves no protective film over the anodic portion as is the case in water. Metals are known to corrode more readily in sodium chloride solution than in that of other salts. Two papers¹ may be found on the corrosion of metal anodes in different solutions. In the first is a list of salts arranged in "The decreasing order of their metal dissolution." The halides are placed first then sulfates, etc. Iron should follow this tendency and corrode less in sodium sulfate solution than in sodium chloride.

When iron dissolves in water or salt solution, monatomic hydrogen is produced at the cathodic area. If this monatomic hydrogen accumulates, it sets up a back E.M.F. which tends to prevent the solution of the iron. Ordinarily the dissolved oxygen serves as a depolarizer for this hydrogen; other substances might be used instead. In these experiments nitrobenzene

¹ E. P. Schoch and C. P. Randolph: *J. Phys. Chem.*, **14**, 719 (1910); G. R. White: **15**, 766 (1911).

serves as a depolarizer. If iron corrodes more readily in a sodium chloride than in sodium sulfate solution, more nitrobenzene should be reduced in the former than in the latter.

A mixture of 35 grams of powdered gray iron and 175 cc. of a solution containing 21 grams of sodium chloride was placed in a round bottom flask and boiled under a reflux for 9.5 hours. The same procedure was followed for the sodium sulfate using the same number of equivalents of this salt. A run with no dissolved salt gave only traces of aniline. This is due to the nature of the film on the iron.

To determine the amount of reduction products the method devised by Allen¹ was used with some modifications. The reduction products and unchanged nitrobenzene were extracted with benzene and filtered off from the iron and iron oxide on a Buchner funnel, and the extract made up to a definite volume. To determine aniline, 10 cc. of the benzene extract were shaken with 150 cc. of dilute sulfuric acid, 5 to 150, in three portions. The acid solution was made up to a definite volume and ten cc. portions titrated using the following standard method. A standard solution of potassium bromate was added to the solution of aniline containing potassium bromide. In the presence of acid the bromate solution liberates bromine and tribromaniline is formed. After the aniline is used up, the bromine color appears. Potassium iodide is added and the iodine liberated by the excess bromine is titrated with a standard solution of sodium thiosulfate.

To determine the total amount of unchanged nitrobenzene and reduction products, 2 cc. portions of the benzene extract were allowed to evaporate at room temperature. The evaporating dish was weighed at regular time intervals. At the point where the benzene disappeared, there was a considerable change in evaporation rate. Allen plotted these results in the form of a curve and from the break in the curve the amount of residue was determined. However, there was a sharp enough change in the rate of evaporation so that a definite weight could be determined without plotting the curve which was sufficiently accurate.

The unchanged nitrobenzene was determined by evaporating 2 cc. portions, as above. The residue was shaken with a large excess, five or six times as much as required, of alkaline ferrous hydroxide. The shaking was continued for half an hour. This process changes the nitrobenzene to aniline but does not change the other reduction products. The mixture was shaken with benzene and the ferrous hydroxide filtered off and washed with benzene on a Buchner funnel. The benzene extract is shaken with dilute sulfuric acid, as mentioned above and the aniline titrated. Knowing the amount of aniline in the residue the amount coming from the reduction of nitrobenzene can be calculated. Subtracting the sum of the weights of the aniline and the nitrobenzene from the weight of the residue, gives the weight of the other reduction products. Using a known sample of nitrobenzene, it was not possible to recover it as aniline without losing 5 to 10%. This would make

¹ J. Phys. Chem., 16, 131 (1912).

the values for nitrobenzene lower than they should be and the values for the other reduction products larger than they actually are.

The results for the above mentioned runs follow:

| Salt | Na ₂ SO ₄ | NaCl |
|---------------------------------|---------------------------------|------|
| Wt. of aniline | 12.3 | 15.5 |
| Wt. of nitrobenzene | 12.5 | 7 |
| Wt. of other reduction products | 5.4 | 5.5 |
| Total wt. recovered | 30 | 28 |

The sodium chloride is more effective in producing reduction. However the difference between the two is not large. Iron, then corrodes to only a slightly less extent in sodium sulfate solution than in sodium chloride.

Snowdon¹ has done considerable work on reduction of nitrobenzene in a manner similar to the one used in the above experiments. He reduced by stirring a mixture of nitrobenzene and different salt solutions in contact with sheet iron. The mixture was kept at a temperature of about 100° by a bath of boiling water.

For most of his work he used ferrous chloride solutions but some runs were made with ferrous sulfate and sodium chloride which are of interest here. Ferrous chloride was found to be considerably more effective than an equivalent amount of ferrous sulfate and in sodium chloride solution there was scarcely any reduction. This does not seem to agree with the results obtained above, so it was thought advisable to try reduction in the presence of ferrous chloride and ferrous sulfate in a manner similar to the one used with the sodium chloride and sodium sulfate solutions. Snowdon used 30 grams of nitrobenzene instead of 35 grams, otherwise the amounts of material are the same. The results are tabulated together with those of Snowdon, in the table below:

| Iron in Solution | Snowdon | | Snowdon | | Snowdon | |
|--------------------------|-------------------|-------------------|-------------------|-------------------|----------------------------|----------------------------|
| | 10 | 10.6 | 10 | 10.6 | Cl as in FeCl ₂ | Cl as in FeCl ₂ |
| Salt | FeCl ₂ | FeCl ₂ | FeSO ₄ | FeSO ₄ | NaCl | NaCl |
| Tot. wt. recovered | 27.5 | | 31 | | 28 | |
| Aniline | 11.1 | 18.5 | 11.5 | 4.7 | 15.5 | .9 |
| Nitrobenzene | 5.7 | 1 | 13.2 | 15.6 | 7 | 27.4 |
| Other reduction products | 10.7 | | 6.5 | | 5.5 | |
| Time—hours | 9.5 | 6.5 | 9.5 | 7 | 9.5 | 7.4 |

It can be seen that the results do not agree with those of Snowdon, as in ferrous chloride and ferrous sulfate solution practically the same amount of reduction was produced and the sodium chloride is more effective than either of these.

¹ J. Phys. Chem., 15, 797 (1911).

Snowdon advanced the theory that the effect of the ferrous chloride was to keep the iron active as the amount of this salt in solution remains practically unchanged. The ferrous chloride is a reducing agent and as reducing agents are known to keep metals active, its effect here would be due to that reason.

However, from the results above it seems as if all that is necessary is an electrolyte which serves, as mentioned before, to change the nature of the film on the iron.

After running the above experiments it occurred to the author that the 30 grams of iron was not sufficient for the reduction of the 35 grams of nitrobenzene. Very little iron remains after reduction in ferrous chloride and ferrous sulfate solution. A larger amount is left when sodium chloride and sodium sulfate is used. This would seem logical if, in the presence of either of the ferrous solutions, the iron corrodes only to the ferrous condition. Both of these solutions being reducing agents they should tend to keep the iron in the ferrous condition. This would require more iron for a given amount of reduction. In the case of the sodium chloride and sodium sulfate the iron would corrode to the ferric condition thus requiring less iron for reduction. The oxide produced has a different appearance in the two cases. From the ferrous salt solutions a black oxide is produced while from the sodium salt solutions it is brown, more the color of ordinary ferric hydroxide.

Three runs were then made using 50 grams of iron powder. Otherwise conditions were the same as in the other runs. Appreciable amounts of iron remained at the end of the run even when ferrous chloride and ferrous sulfate were used. A much larger amount was left when sodium chloride was used.

TABLE II

| Salt | FeCl ₂ | FeSO ₄ | NaCl |
|--------------------|-------------------|-------------------|------|
| Tot. wt. recovered | 27 | 26 | 29 |
| Aniline | 24.8 | 22.6 | 19 |
| Nitrobenzene | | .4 | 3 |
| Other products | | 3 | 5 |
| Time—hours | 9 | 9 | 9.5 |

The order of the amount of reduction with the different salts agrees with that of Snowdon. Using ferrous chloride and ferrous sulfate there was practically complete reduction as 24.8 grams of aniline is equivalent to 32.8 grams of nitrobenzene. The amount of reduction using sodium chloride, has also increased but not in a corresponding amount. Here it is not a question of a sufficient amount of iron but the reduction process is speeded up, due to the increased surface of the iron.

The results still differ widely from those obtained by Snowdon. It was thought that the kind of iron used might have some effect on the amount of reduction produced. The gray powdered iron used in the preceding experiments would contain most of its carbon in the graphitic form and, as mentioned before, this iron dissolves more readily than iron which contains

iron carbide. Snowdon used sheet iron which would probably contain considerable iron carbide. Strips of sheet iron were used in the following runs which contains all its carbon in the combined form.

TABLE III

| | I | II | III | IV | V | VI |
|--------------------|-------------------|-------------------|------|------|------|---------------------------------|
| Amount of iron | 40 | 42 | 38 | 30 | 36 | 45 |
| Salt | FeCl ₂ | FeSO ₄ | NaCl | NaCl | NaCl | Na ₂ SO ₄ |
| Tot. wt. recovered | 20 | 30 | | 31 | 34 | 33 |
| Aniline | 16.9 | 10.8 | 2.2 | 2.9 | 2.6 | 1.6 |
| Nitrobenzene | none | 10.7 | | 19.5 | 22.4 | 26.2 |
| Other products | 3 | 8.5 | | 8.6 | 8.9 | 5.2 |
| Time—hours | 9 | 8 | 9.5 | 9.5 | 15 | 9.5 |

Here the results agree fairly well with those of Snowdon. The most reduction occurs with ferrous chloride, somewhat less with ferrous sulfate, while sodium chloride and sodium sulfate bring very little reduction. The iron strips from the ferrous solutions come out clean while from the other two they come out covered with a deposit of adherent rust. This is an indication of the tendency of the former solutions to keep the iron active while the rust on the iron from the latter would tend to cut down the action.

The iron loss in the reduction using ferrous chloride solution was 20 grams which proves the point mentioned above, that 30 grams of iron is not sufficient for reducing the 35 grams of nitrobenzene.

When iron strips are used the total surface exposed would be considerably less than if the same amount were present as iron powder. To determine the effect of surface exposed, some of the iron strips were made into turnings and run IV made with these. This does not increase the amount of reduction to a very great extent. The greater reduction with the gray iron powder, then, is not due to its greater surface but to the nature of the iron. This is borne out in actual practice,¹ where gray iron filings are used. It is stated that particles of steel which have become mixed with the iron are found unchanged at the end of the action.

TABLE IV

| | I | II | III |
|--------------------|------|------|------|
| Iron | 30 | 30 | |
| Tot. wt. recovered | 29 | 28 | 33 |
| Aniline | 17.7 | 15.5 | 6.3 |
| Nitrobenzene | 3.8 | 7 | 20.8 |
| Other products | 7.5 | 5.5 | 6 |
| Time—hours | 16 | 9.5 | 9 |

¹ P. R. Groggins: "Aniline and its Derivatives".

Some runs were made to see if the iron did eventually go passive in sodium chloride solution. If it goes passive, increasing the time of heating should not increase the amount of reduction; also the iron left after one reduction should not be capable of further action if used again.

Gray iron powder was used for these experiments.

It will be seen from the results that there is some increase in the amount of aniline produced by boiling for about seven hours longer. The action is slowed up because the iron becomes coated with oxide. The free oxide that accumulates would also tend to settle down on the iron thus retarding its action. In run III the iron left after a run with 50 grams of iron was used again. There was some reduction which indicates that the iron has not gone passive but is not as effective as it was when first used.

Two runs were made with strips of the sheet iron and sodium chloride which also have a bearing on the above. In one case glass beads were placed in the flask with the iron strips. These rubbing against the iron should tend to keep it active. In the other run the iron strips were taken out three times during the course of the action, cleaned and rubbed with sandpaper. In neither case is there any appreciable increase in the amount of aniline produced. This indicates that the iron remains active, for this treatment should activate it if it had become passive thus increasing the aniline yield.

Snowdon also performed another experiment which is not in accordance with those of the author. He states that if strips of iron are placed in a flask and a mixture of boiling ferrous chloride solution, hydrochloric acid and nitrobenzene is kept in contact with it for some time that no appreciable reduction of the nitrobenzene occurs. He explains this as due to the insufficient contact of the nitrobenzene with iron. Better contact is obtained in his other runs by stirring. In the runs with iron strips made by the author, the conditions were exactly the same except for the presence of hydrochloric acid. Here reduction takes place as can be seen from the results in Table III. The explanation of Snowdon's results may be found to be due to the position of the iron strips in the flask. If they were not small enough to fit in the bottom of the flask where the nitrobenzene layer is, there would be little contact between the two, therefore little reduction.

Passivity of Tin in Nitric Acid

Considerable work has been done on the passivity of metals. A good summary of this work is given by Dunstan and Hill.¹ The different theories of passivity are mentioned with the conclusion that the oxide theory is the most generally accepted. Their own work favors the oxide theory. The passivity of other metals was also studied. Bancroft favors the oxide theory but believes it to be a higher oxide, not stable in itself, which is adsorbed by the metal.

In an article,² Schon states that tin becomes passive in nitric acid, sp. gr. 1.42, when in contact with platinum, but without platinum energetic decom-

¹ J. Chem. Soc., 99, 1853 (1911).

² Z. anal. Chem., 10, 291 (1871).

position takes place. Cadmium behaves similarly, only a more concentrated acid, sp. gr. 1.47, must be used before it will become passive even with platinum. The function of the platinum would be to act as cathode thus liberating hydrogen at its surface rather than at the surface of the tin where it would tend to reduce the oxide film to which the passivity is due. Hydrogen has a lower overvoltage on platinum which would make it a less powerful reducing agent even if it did come in contact with the oxide of tin.

Faraday¹ has done similar work with iron and finds that it will go passive in nitric acid when in contact with platinum and also if the platinum is simply connected with the iron.

It was thought that the passive film on the tin might be stannic nitrate as this is produced as an insoluble substance when tin is acted on by concentrated nitric acid.² Two experiments show that this is not the case. Stannic nitrate is soluble in water so if this is the passive film, it should be removed when the tin is placed in water. A rod of tin was made passive by action of nitric acid and then shaken in warm water for a few minutes, dried and put back in nitric acid of such strength that it would be attacked if not passive. It still remains passive, showing that the film is not soluble stannic nitrate. There is, however, a possibility of the stannic nitrate being adsorbed by the tin so that it would not dissolve in the water. To disprove this, tin was made passive by making it anode in sodium hydroxide solution. It was washed and dried, then placed in a concentration of nitric acid in which it would ordinarily be attacked. The tin remains passive which indicates the passive film is not stannic nitrate.

The method used in the following experiments on passive tin is as follows: Nitric acid, of the desired specific gravity, is made up by diluting the fuming acid. The strength of the diluted samples was determined by titrating a definite weight of the acid with standard sodium hydroxide solution. To insure that the tin was active each time it was dipped in the nitric acid, it was allowed to stand in hot hydrochloric acid and then washed and dried before being placed in the nitric acid.

Tin, at ordinary temperatures, will go passive even when not in contact with platinum, in nitric acid, sp. gr. 1.46. At a concentration of sp. gr. 1.456 it is slowly attacked. When a spiral of platinum wire is wound around the tin rod it will go passive in an acid as dilute as sp. gr. 1.426 but begins to be attacked slowly at sp. gr. 1.423.

Platinum should have the same effect in making tin passive if it were connected with a platinum electrode. The platinum electrode is connected to the tin rod and both are immersed in the nitric acid about 2 or 3 cm. apart. Some experiments were tried using nitric acid of the same strength as used with the platinum wire but passivity is not produced. A higher concentration, sp. gr. 1.442, will produce passivity. The increased concentration necessary to produce passivity is due to the resistance of the solution. It follows

¹ "Experimental Researches", 2, 240.

² Mellor: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", 7, 330 (1927).

that if the distance between the tin and the platinum is increased, the tin would have more of a tendency to remain active. The same effect could be produced by putting a resistance in the external circuit. A slide wire resistance was then placed in the circuit. Using about 3 ohms resistance the tin still becomes passive at sp. gr. 1.443. If the resistance is increased to 6 ohms the tin remains active.

Tin may also be made passive by making it anode in a nitric acid solution. A cathode of platinum was used and kept 2 or 3 cm. from the anode. Storage batteries served as the source of current, 9.6 volts being the E.M.F. employed. When the current was first applied a large ammeter reading was registered for an instant. This drops quickly back to a very small value, around .005 ampere, due to the formation of the passive film. Using this source of current tin went passive in an acid as dilute as sp. gr. 1.344. At sp. gr. 1.34 it remained active. Using 5.5 volts it will not go passive in ordinary concentrated nitric acid, sp. gr. 1.407. The same is true using 3.6 volts.

It is evident then, that a rather high E.M.F. must be applied to make a tin anode passive. The function of the current would be to overcome the solution resistance making it easier to discharge hydrogen at the cathode. Also, as the E.M.F. applied is raised it becomes easier to discharge oxygen at the anode which would aid in the formation of the passive oxide film. This would explain why the smaller E. M. F. does not produce passivity.

Krassa¹ deals with a somewhat similar case, the formation of passive iron by making it anode in alkali. In boiling alkalies the passive state is quickly attained with strong currents and no visible alteration of the surface is produced. With weak currents, however, a visible film of oxide is first produced which attains considerable thickness before passivity is arrived at. He explains this as due to the formation of a complete thin film of oxide by the strong current. With weak currents the film is more irregular, so greater thickness is required before it becomes complete.

The same idea can be applied to the tin anode in nitric acid. A thin complete film forms with a strong current while with weak currents the film never becomes complete enough to produce passivity. Of course the better film with the stronger current is undoubtedly due to the action of the increased amount of nascent oxygen produced.

Summary

The results obtained in this investigation may be summarized as follows:

(1) Total carbon may be determined by an electrolytic method, making the iron anode in sodium sulfate solution.

(2) Graphitic carbon cannot be determined by making iron cathode in an ammoniacal ammonium nitrate solution. The current does not cause the corrosion and it is therefore slow and leaves total carbon (not graphitic carbon).

¹ Z. Elektrochemie, 15, 490 (1909).

(3) Depolarizers added to iron dissolving in acid raise the amount of carbon remaining. Using potassium permanganate with white iron this can be brought up to the total carbon content, while it is somewhat less with gray iron due to the oxidation of the graphitic carbon by the permanganate. Chlorine and aqua regia also raise the amount of carbon remaining.

(4) 25% tin added to molten gray cast iron throws carbon out of the iron but not the total graphitic carbon content as claimed by Eyferth. The formation of two layers with increasing amounts of tin makes the addition of more tin, beyond a certain amount, have little effect. Carbon is present in molten iron either as dissolved carbon alone or there is an equilibrium existing between it and iron carbide. The high combined carbon of the alloy is explained as due to the dissolving of the silicon by the tin.

(5) Aniline added to sulfuric acid cuts down the hydrogen evolved by iron to a large extent. This does not prevent the acid from removing mill scale. The presence of the aniline raises the hydrogen overvoltage on the iron.

(6) Gray iron will reduce nitrobenzene to about the same extent when boiled with either sodium chloride or sodium sulfate solutions. This indicates that both are effective in keeping iron active. The results found were not in accordance with those obtained by Snowdon. This was found to be due to the kind of iron used. Iron does not go passive in sodium chloride solution during the course of the action.

(7) Tin goes passive in nitric acid when wrapped with a platinum wire. This is caused by the liberation of the hydrogen from the platinum. Connected to a platinum electrode it goes passive, but in a more concentrated acid, because of the increased solution resistance. It also goes passive when made anode in an acid more dilute than that used with the platinum wire. Passivity in this case is brought about by the discharge of hydrogen at the cathode and the effect of the nascent oxygen at the anode.

Acknowledgment

This investigation was carried out under the supervision of Professor W. D. Bancroft. The writer wishes to take this occasion to express his appreciation of the suggestions and constructive criticisms offered. He feels that it is a rare privilege to have had the opportunity of associating with Professor Bancroft during this work.

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NEW BOOKS

Soil Conditions and Plant Growth. By Edward J. Russell. Fifth edition. 22 × 14 cm; pp. viii + 516. New York and London: Longmans, Green and Co., 1927. Price: \$6.50. The preceding edition was reviewed about six years ago (26, 292). In the preface the author says, p. v: "Perhaps the most striking advances since 1921 have been in the chemistry of the soil. Once more the general rule in scientific progress has been exemplified. The study of the soil was for long supposed to be entirely a matter for chemists. Then came the brilliant investigations of the bacteriologists which brought soil microbiology very much to the fore; soil physics also came into great prominence and soil chemistry fell into the background. This was not the result of caprice on the part of investigators; soil chemistry had gone as far as its methods allowed, and it was brought to a standstill by the sticky colloids of the soil. But with the development of methods for studying colloids in laboratories devoted to pure science, further possibilities of advance in soil chemistry have been opened up, and these have been eagerly seized by enthusiastic workers in Europe, America, and elsewhere. Once again it has been shown that progress in applied science is limited by the state of knowledge of pure science, and that the surest way of solving technical problems is to investigate the underlying principles and causes."

"All branches of the subject have advanced, however, and it has been necessary to re-write all except the historical portions of the book."

It is quite extraordinary to see how good a guess Palissy made in 1563. "You will admit that when you bring dung into the field it is to return to the soil something that has been taken away. . . . When a plant is burned it is reduced to a salty ash called alcaly by apothecaries and philosophers. . . . Every sort of plant without exception contains some kind of salt. Have you not seen certain labourers when sowing a field with wheat for the second year in succession, burn the unused wheat straw which had been taken from the field? In the ashes will be found the salt that the straw took out of the soil; if this is put back the soil is improved. Being burnt on the ground it serves as manure because it returns to the soil those substances that had been taken away," p. 1.

"Liebig's famous report to the British Association on the state of organic chemistry came like a thunderbolt upon the world of science. With polished invective and a fine sarcasm he holds up to scorn the plant physiologists of his day for their continued adhesion, in spite of the accumulated evidence, to the view that plants derive their carbon from the soil and not from the carbonic acid of the air. "All explanations of chemists must remain without fruit, and useless, because even to the great leaders in physiology, carbonic acid, ammonia, acids, and bases, are sounds without meaning, words without sense, terms of an unknown language, which awake no thoughts and no association." The experiments quoted by the physiologists in support of their view are all "valueless for the decision of any questions." "These experiments are considered by them as convincing proofs, whilst they are fitted only to awake pity." Liebig's ridicule did what neither de Saussure's nor Bous-singault's logic had done; it finally killed the humus theory. Only the boldest would have ventured after this to assert that plants derive their carbon from any source other than carbon dioxide, although it must be admitted that we have no proof that plants really do obtain all their carbon in this way," p. 15.

"The failure of the patent manure was not entirely the fault of the theory, but only affords further proof of the numerous pitfalls of the subject. The manure was sound in that it contained potassium compounds and phosphates (it ought of course to have contained nitrogen compounds), but it was unfortunately rendered insoluble by fusion with lime and calcium phosphate so that it should not too readily wash out in the drainage water. Not till Way had shown in 1850 that *soil precipitates soluble salts of ammonium, potassium, and phosphates* was the futility of the fusion process discovered, and Liebig saw the error he had made," p. 18.

"The general conclusion that bacteria are the real makers of plant food in the soil, and are, therefore, essential to the growth of all plants, was developed by Wollny and Berthelot. It was supposed to be proved by Laurent's experiments in 1886. He grew buckwheat on humus obtained from well-rotted dung, and found that plants grew well on the untreated humus, but only badly on the humus sterilised by heat. When, however, soil bacteria were added to the sterilised humus (by adding an aqueous extract of unsterilised soil) good growth took place. The experiment looks convincing but is really unsound. When a rich soil is heated, some substance is formed toxic to plants. The failure of the plants on the sterilised humus was, therefore, not due to absence of bacteria, but to the presence of a toxin. No one has yet succeeded in carrying out this fundamental experiment of growing plants in two soils differing only in that one contains bacteria while the other does not," p. 27.

"Some interesting results are obtained in glass house practice. Tomato growers have learned to regulate water supply and temperature in such a way as to produce compact bushy plants, which they know by experience give more fruit than the softer, larger plants, obtainable under other conditions. Until the blossom is fertilised or has set, therefore, vigorous growth is not encouraged, and, in many cases, while the atmosphere is artificially damped, water is actually withheld from the roots until, in the picturesque language of the grower, "the plants cry for it." After "setting", water is liberally supplied and top dressings of manure are given. Analysis of these effects has been begun. R. A. Fisher and his colleagues have studied by statistical methods the effect of rainfall and hours of sunshine on the yields of wheat and barley at Rothamsted and F. G. Gregory has used growth rates successfully in studying the influence of climate on the growth of barley. Gregory brings out the important point that the different physiological processes making up plant growth are differently affected by changes in external conditions and thus tend to compensate one another so that the total change in growth is less than might be expected. Thus assimilation per unit area of leaf (net assimilation rate, p. 48) increases or is positively correlated with increasing temperature and radiation up to a point, while rate of growth of leaf area is negatively correlated with it. In fine weather the assimilation is good, but the leaf growth is poor; in poor weather the assimilation is less, but the leaf growth is better; variations in season, therefore, make less difference than might be expected," p. 58.

"It is well known among farmers and gardeners that soil aeration is essential to fertility, but exact measurements are difficult to obtain. The phenomena are more complex than appears at first sight, involving two wholly distinct factors:—

1. The necessity of a supply of oxygen to the plant root.
2. The toxic effect of the carbon dioxide which invariably accumulates in a non-aerated soil or other medium.

"Plants vary considerably in their sensitiveness to these factors. They do not all stand in equal need of oxygen for their roots. E. E. Free grew buckwheat in water cultures, blowing air through one set, and nitrogen, oxygen, and carbon dioxide respectively through others. The plants supplied with nitrogen were indistinguishable from those supplied with air or oxygen: they all grew normally to maturity. Buckwheat roots, therefore, apparently need but little gaseous oxygen. When, however, carbon dioxide was given the plants sickened and wilted within a few hours and died in a few days. Barley, on the other hand, is more sensitive to deficient oxygen supply," p. 63.

"The nutrition of plants is complicated by the fact that plants synthesise their own food from various substances taken out of the air and the soil. It is common in farmers' lectures to speak of these as the actual foods, but the student must be perfectly clear in his own mind that they are only the raw materials out of which the food is made. It is convenient to make a distinction between the elements necessary in large quantities and those of which mere traces suffice: the effect of the former can readily be demonstrated in water and sand cultures; the latter are more difficult to study as traces are always present in the seed, and often also in the nutritive medium, or the vessel in which the plant is grown.

"The substances needed in quantity are carbon dioxide, water, oxygen, and suitable compounds of nitrogen, phosphorus, sulphur, potassium, calcium, magnesium, and iron. Of these nitrogen, phosphorus, and potassium compounds are required in such large amounts

that they usually have to be added to soils as artificial fertilisers in order to obtain maximum yields in agricultural practice. The other nutrient elements are generally present in air, in soils or in rain, in sufficient amounts to exert their full effect, though cases are recorded where crops have responded to additional supplies of sulphates and magnesium. The function of these nutrients is to build up the plant substances.

"A second group of substances is needed in small amounts only. These have been studied at the Institut Pasteur, notably by Gabrielle Bertrand and by Mazé; also by Dr. Brenchley at Rothamsted. The elements proved to be essential are iron, manganese, and, for certain crops, boron. Others probably always present in the plant are fluorine, iodine, chlorine, copper, aluminium, zinc, cobalt, and nickel; it is not known whether they serve some useful purpose or have simply been absorbed along with the nutrients proper. The essential elements of this group apparently serve two purposes:—

1. Catalytic, the promotion of oxidation or the essential reactions;
2. Stimulative, the setting in train of differentiations or other processes vitally important to the plant.

"The catalytic elements probably include iron, which is essential to the formation of chlorophyll; manganese, apparently needed for the activation of oxydases or otherwise for oxidations in the plant; silicon, which somehow increases the effectiveness of phosphate and possibly also of potassium. The stimulative elements probably include boron, needed to stimulate the formation of the branch system of circulatory vessels that links up the nodules on the roots of leguminous plants with the main system," p. 70.

"Phosphate starvation affects markedly the composition of crops, lowering their nutritive value to animals and their special quality values to men. Over large areas of the world, soils are very deficient in phosphate. Those occurring in parts of South Africa carry a natural herbage which causes deficiency disease in cattle; the affected animals devour bones with great eagerness, even putrefying bones when the deficiency is pronounced, so that they become liable to a particular ptomaine poisoning. The obvious remedy is to feed the cattle with bone meal. Similar diseases occur in Australia, where also the arable land shows astonishing benefits from small dressings of superphosphate. In the Romney Marsh the best fattening pastures are richer in phosphate than the poorer ones; this is generally true of England and France. Paturel has shown that the best wines contain most P_2O_5 (about 0.3 gm. per litre), the second and lower qualities containing successively less. Further, when the vintages for different years were arranged in order of their P_2O_5 content a list was obtained almost identical with the order assigned by the wine merchants. Davis has emphasised the importance of phosphate supply for the indigo crop," p. 81.

"The conception of the clay "molecule" that is provisionally put forward as a working hypothesis, and in the full expectation that it will be seriously modified, if not entirely overturned, by subsequent work, is somewhat as follows:—

"The particles are perforated like sponges so that their surface is much greater than would be expected from their diameters. When suspended in water they become surrounded by a double electric layer; the outer one consists of the positively charged cations (mostly Ca^{++} , but with some Mg^{++} and smaller quantities of K^+ , Na^+ , H^+ , etc.), the inner with negatively charged anions, a complex aluminosilicic acid of unknown constitution, but obeying the usual stoichiometrical laws. Some of the cations split off by dissociation, leaving a balance of negative charge. Changes in the cations are accompanied by changes in the physical properties of the clay. Wiegner supposes that a cation linked up with many molecules of water, such as sodium, could not approach the complex anion as closely as cations which are less hydrated, like calcium; the effective distance between the two electric layers is increased and the potential of the inner layer increases. This increased potential increases the power to remain suspended in water and the chemical instability. This view accords with Gedroiz's results that cations are absorbed in the order of their valencies, and within the valency groups of their atomic weights. Thus aluminium is of all cations the one most readily absorbed, giving the most compact deposit in water: calcium is less readily absorbed giving a more bulky deposit, but sodium and lithium are least easily absorbed; they give the bulkiest and most hydrophilous deposit, having also the finest particles (see p. 131).

and the cations are most easily lost by hydrolysis. This explains why among the replaceable bases of normal soils, calcium occurs in larger quantity than magnesium, which, in turn, is in larger quantity than potassium, while sodium is least common and may be absent: it explains also why sodium is the predominating ion in sea water," p. 152.

"Peat shows the phenomenon of swelling in a marked degree; indeed, after heavy rainfall inadequately-drained peat bogs may swell so much as to overflow into valleys with disastrous results. After drainage, however, drying and shrinkage set in, followed by a slow but steady erosion as air penetrates into the newly-formed spaces and starts the oxidation processes. When Whittlesey Mere was drained in 1851 a pillar was driven through the peat into the underlying gault, and the top of the pillar was made flush with the surface of the soil. So great has been the subsequent shrinkage that over ten feet of the pillar is now out of the ground and the process has not yet reached its limit, for a perceptible further shrinkage took place during the dry season of 1911," p. 160.

The author accuses Langmuir, p. 198, of saying that surface actions "are shown to obey the ordinary stoichiometric laws and they can be thought of as simple chemical changes." What Langmuir did say was that the forces acting in adsorption are chemical; but he never said, so far as the reviewer knows, that the relations are stoichiometric.

"The values for drawbar pull promise to have considerable value in soil science. They afford a measure of tilth; they are of obvious importance to the implement maker; and they give the best measure we have at present of the resistance of the soil to the movement of plant roots. They constitute an integration value for the clay properties; thus they are closely related to the rate of efflux of water from the drains laid two or three feet below the surface of the soil," p. 225.

"The mode of entry of the organism into the plant was studied, first by Prazmowsky for the pea, afterwards by Nobbe and Hiltner, Marshall Ward, and Miss Dawson, who described the morphological changes; there is also much later work. The first step is that the organism attaches itself to a root hair near the tip and multiplies rapidly, softening the cell walls (shown by the curling over of the end of the hair) and thereby facilitating the entry of the organisms. But the bacteria cannot wander at will through the plant; they are confined by some mechanism not yet known to a slimy filament which grows down the interior of the root hair, penetrating the cell walls by some unknown means, till they reach the inner layer of the cortex of the root. The adjacent cells at first multiply to form a mass of small cells which constitute the nodule; but these small cells, once they are entered by the bacteria, cease to divide and instead they enlarge considerably. Only at the distal end do the cells remain uninfected, and these continue division so that the nodule elongates.

"The organisms are not yet, however, in connection with the circulating system of the plant, and until they are the symbiosis is not effective. Connection is established by vascular strands which grow out from the stele and surround the swollen cell tissue. Along these new vessels pass sugars and other nutrients and sources of energy from the plant to the organism, and the synthesised nitrogen compounds from the organism to the plant," p. 281.

"So far as the writer can discover, the only record of soil or dust absolutely free from living organisms is the dust from a newly opened 18th dynasty Egyptian tomb which had been left dry and undisturbed for over three thousand years," p. 296.

"The entire stock of nitrate in the soil at any time appears to occur in the soil solution, and it is liable to be washed out completely by heavy rain; in any case little if any survives the winter. In favourable conditions fresh supplies are soon produced, but after a wet winter, when the soil is cold and poorly aerated, nitrification may be slow. Crops then show a marked response to dressings of sulphate of ammonia, nitrate of soda or nitrate of lime. Very little ammonia appears in neutral soil, it being readily absorbed by the colloids and assimilated or oxidised by micro-organisms," p. 370.

"On certain sour soils in Yorkshire farmers tend to confine themselves to oats, potatoes, and rye, and do not attempt barley or red clover. Near Leeds, where even the rain water is acid, rhubarb is grown extensively," p. 382.

"Serious soil exhaustion did not arise under the old agricultural conditions where the people practically lived on the land and no great amount of material had to be sold away from the farm. Phosphate exhaustion was the most serious occurrence because there was no way of meeting it, and as the original supplies were not as a rule very great, it must have become acute by the end of the eighteenth century in England, for remarkable improvements were, and still are, effected all over the country by adding phosphates. Then began a process, which has gone on to an increasing extent ever since, of ransacking the whole world for phosphates; at first the search was for bones, even the old battle-fields not being spared, if we may believe some of the accounts that have come down; later on (in 1842) Henslow discovered large deposits of mineral phosphates, to which more and more attention has been paid. Phosphate supplies may yet become the factor that will determine the course of history," p. 433.

Wilder D. Bancroft

General Chemistry. By Azariah T. Lincoln and George B. Banks. 22 × 16 cm; pp. v + 681. New York: Prentice-Hall, Inc., 1928. Price: \$3.50. In the preface the authors say, p. iii: "This book is offered by the authors as a textbook for students in a first year college course in chemistry. It is written along the lines of a method based upon the arrangement of the elements in the electrochemical series, which they have used in their classes during the last few years."

In spite of this method the order of the forty-three chapters is practically the same as that found in many of the older texts. Most of the theories are introduced in connection with the study of the non-metals; while the study of the metals covers only five chapters. Colloids constitute chapter fourteen. "There has been included a much more extensive discussion of organic chemistry than is usual in textbooks for a first year college course. In this is given the chemistry of those substances which constitute our food, clothing, and shelter, and which contribute so much to our pleasures. This knowledge, of vital interest to everyone, is due to the large number of students who do not study chemistry for more than one year," p. iv.

The book makes an impression of being up-to-date and many of these modern applications are illustrated. The index is quite complete, covering twenty-eight pages. The mathematical side of the subject is stressed very lightly while the descriptive side is emphasized.

This text will not be satisfactory to that group of chemistry teachers who insist on teaching as they were taught. It will not lend itself to use for recitation purposes unless amplified by lectures. This is true in spite of the facts that the book is well and concisely written and is characterized by the inclusion of some mention of most of the important subjects in chemistry. This comprehensiveness is at once the book's strength and weakness, depending on the teacher and the character of the course he is giving. It is a weakness in that no normal first year student could be expected to grasp and retain the multitude of facts and theories assembled. The teacher must resort to repeated omissions or a general cursory treatment and either expedient is weak pedagogically. The book will probably serve best as a reference text or as a text in courses where ample time is allotted for such an extensive study.

This same comprehensiveness will be a merit in the eyes of those teachers who are working out cultural courses in chemistry. The average student of this text may conclude his study with a much less thorough grounding in fundamental chemical theories and concepts than was formerly thought necessary, but he should certainly know *about* many more facts and applications than used to be covered in the first course. The text seems to approach somewhat toward the ideal of a cultural course in chemistry as outlined recently by Prof. Bancroft under the title, *Pandemic Chemistry*. It may mark the beginning of a new era in the teaching of chemistry for it is certainly different from its predecessors.

Herbert L. Davis

SIXTH REPORT OF THE COMMITTEE ON CONTACT CATALYSIS¹

BY ROBERT E. BURK*

As indicated by Chemical Abstracts, the volume of research in 1927 upon the theory of contact catalysis has not been enormous, many of the workers having been led into investigations of closely related fields, such as the general theory of reaction velocity, adsorption, etc. At the same time, important, newly-developed catalytic processes in industry, such as the synthesis of petroleum² and of methanol,³ progress in the study of enzymes,⁴ etc., have rendered still more urgent the searching out of the mechanism of catalysis.

The present report, in addition to covering important new developments of the year in catalysis, summarizes the principal points of the five previous reports.⁵ An attempt is also made to summarize relevant work in other fields, which has come to our notice, with the hope that the contributing factors to catalytic phenomena will be thrown into somewhat sharper relief. These purposes are necessarily incompletely fulfilled.

Two books of interest to catalytic investigators should be mentioned. A new edition of Rideal and Taylor's "Catalysis in Theory and Practice" contains extensions and improvements and is well worth reading. The general plan of the book is good, and some of the chapters, for instance that on "promoters," contain valuable information not readily found elsewhere. The theoretical treatment did not leave the writer with a feeling of very great satisfaction.

The second book is a German translation of the second French edition of Sabatier's "Catalysis in Organic Chemistry," by B. Finkelstein. The translation proper is probably not so valuable to English-speaking readers as is the translation by Professor Reid; for the latter contains a chapter on theories of catalysis, many footnotes, and is arranged in better form. The new German volume, however, contains a summary by H. Hauber of catalytic literature between the years 1920 and 1926.

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¹ Report of the Committee on Contact Catalysis of the Division of Chemistry and Chemical Technology of the National Research Council. Written by R. E. Burk with the assistance of the other members of the committee: Messrs. H. A. Adkins, E. F. Armstrong, O. W. Brown, C. G. Fink, J. C. W. Fraser, J. N. Pearce, E. E. Reid, H. S. Taylor, and W. D. Bancroft, Chairman.

² Killeffer: *Ind. Eng. Chem.*, 19, 1077 (1927).

³ Jaeger: *Abhandl. Kenntnis. Kohle.*, 7, 51 (1926); *Chem. Abs.*, 21, 3531 (1927).

⁴ Willstätter: "Problems and Methods of Enzyme Research," Cornell University (1927).

⁵ These five preceding reports are—First Report of the Committee on Contact Catalysis: *Ind. Eng. Chem.*, 14, 326-31, 444-7, 545-8, 642-6 (1922); *Nat. Res. Council Reprint No. 30*, (1922). Second Report of the Committee on Contact Catalysis: *J. Phys. Chem.*, 27, 801-941 (1922); *Nat. Res. Council Reprint No. 50* (1923). Third Report of the Committee on Contact Catalysis: *J. Phys. Chem.*, 28, 897-942 (1924); *Nat. Res. Council Reprint No. 59* (1924). Fourth Report of the Committee on Contact Catalysis: *J. Phys. Chem.*, 30, 145-71 (1926); *Nat. Res. Council Reprint No. 66*, (1926). Fifth Report of the Committee on Contact Catalysis: *J. Phys. Chem.*, 31, 1121-49 (1927); *Nat. Res. Council Reprint No. 78* (1927).

Summary of Previous Reports

From the five previous reports of the Committee on Contact Catalysis, the following points remain unchallenged, so far as I know, and represent the principal features of general experience in contact catalysis.

1. Contact catalysis does not take place unless one or more of the reactants is adsorbed on the surface of the catalyst.¹
2. The complex thus formed on the surface may correspond to a definite orthodox chemical compound as in the case of the decomposition of hydrogen peroxide at a mercury surface,² or it may not correspond to such a compound; for instance, no known oxide of carbon has the chemical properties of oxygen adsorbed on charcoal.³
3. The amount of gas adsorbed on the catalyst and the extent of catalysis do not show quantitative correspondence.⁴
4. Any substance strongly adsorbed on the catalyst will prevent reactants from reaching it, and will thus "poison" the catalyst,⁵ provided the catalytic activity of the poison itself is small. The poison may be one of the reactants in case it is necessary for more than one reactant to be adsorbed upon the surface, as in the case of the poisoning of a platinum wire by carbon monoxide for the catalysis of the combination of this gas with oxygen.⁶ It may be one of the products of reaction, e.g., hydrogen poisons a platinum wire for the catalytic decomposition of ammonia by this metal.⁷ Lastly, the poison may be a foreign substance of which there are many familiar examples such as the effect of sulphur compounds, stopcock grease, etc., upon the catalytic action of platinum.
5. In some cases the amount of poison necessary to completely stop the activity of a catalyst is less than that necessary to cover it with a monomolecular layer.⁸
6. Some catalysts have been shown to have varying saturation capacities for various substances,⁹ and the ratio of the saturation capacities for adsorbed gases on a given substance has been found to vary for different preparations, and for a given sample before and after heat treatment.¹⁰
7. Poisons do not always have a proportionate effect upon adsorption and catalytic activity of the catalyst.
8. The results 5, 6, 7, and others, force the conclusion that some catalysts are not uniformly active.¹¹

¹ Bancroft: First Report of the Committee on Contact Catalysis.

² Bredig and von Antropoff: *Z. Elektrochemie*, 12, 581 (1906); von Antropoff: *J. prakt. Chem.*, (2) 77, 273 (1908).

³ Bancroft: First Report of the Committee on Contact Catalysis.

⁴ Taylor: Third Report of the Committee on Contact Catalysis.

⁵ Discussed in all of the reports of this committee.

⁶ Langmuir: *Trans. Faraday Soc.*, 17, 653 (1922).

⁷ Hinshelwood and Burk: *J. Chem. Soc.*, 127, 1105 (1925).

⁸ Armstrong and Hilditch: *Trans. Faraday Soc.*, 17, 669 (1922).

⁹ Pease: *J. Am. Chem. Soc.*, 45, 2296 (1923); Hurst and Rideal: *J. Chem. Soc.*, 125, 685, 694 (1924).

¹⁰ Maxted: *J. Chem. Soc.*, 127, 73 (1925); Pease: *J. Am. Chem. Soc.*, 45, 2296 (1923); Taylor: Fourth Report of the Committee on Contact Catalysis.

¹¹ Taylor: Fourth Report of the Committee on Contact Catalysis.

9. The power of catalysts to activate molecules is often very specific.¹ A particularly interesting case of the specificity of catalysts is the ability of different catalysts to accelerate the decomposition of a given molecule, e.g., formic acid² in different ways.

10. It is sometimes found that the catalytic activity of a mixture of catalysts exceeds the additive effect of the two. This is called promoter action.³

11. Continued reaction alters the activity of some catalysts, for instance, quartz in the decomposition of ammonia⁴; and causes visible roughening in other cases, for instance, platinum in the catalytic oxidation of sulphur dioxide.⁵

12. Certain substances called "negative catalysts" or inhibitors are found to decrease the rates of supposedly homogeneous reactions.⁶

13. Reactions involving a solid reactant and a solid product are often found to occur at the interface between the two solid phases.⁷

14. Processes such as heat treatment, which might well disturb special configurations of surface atoms are often found to decrease markedly the activity of catalysts.⁸

Theories of catalysis must be consistent with these points.

Contact Catalysis and Reaction Velocity in General

It may be thought that since catalytic phenomena have to do with altered reaction velocities, a solution of the problem must await a satisfactory solution of homogeneous reaction velocity. In answer to this, it may be said, first, that the main paths are blazed in the theory of reaction velocity; secondly, as emphasized all along by Bancroft,⁹ that a great part of the problem of contact catalysis must consist in an analysis of the effect of adsorption upon the adsorbed molecule. Nevertheless, since the subject of contact catalysis deals with changes in reaction velocity, and since solid progress has been made in the study of the latter subject, it is thought desirable for the purposes of this report to summarize briefly the main points in the theory of homogeneous reaction velocity. Much of the work upon this subject has appeared since the first report of this committee was written.

¹ This important point is discussed in all the previous reports of the Committee on Contact Catalysis.

² Adkins and Krause: *J. Am. Chem. Soc.*, 44, 385 (1922); Adkins and Nisson: 45, 809 (1923); 46, 130; Adkins and Lazier: 2291 (1924); Bischoff and Adkins: 47, 807 (1925); Hinshelwood, Hartley and Topley: *Proc. Roy. Soc.*, 100A, 575 (1922); Tingey and Hinshelwood: *J. Chem. Soc.*, 121, 1668 (1922); Hinshelwood and Topley: 123, 1014; Hinshelwood and Hartley: 1333 (1923).

³ Promoter action is also discussed in all of the previous reports of the Committee on Contact Catalysis.

⁴ Hinshelwood and Burk: *J. Chem. Soc.*, 127, 1105 (1925).

⁵ See the photographs in Rideal and Taylor's "Catalysis in Theory and Practice," p. 177.

⁶ See Reid: Fifth Report of the Committee on Contact Catalysis.

⁷ Langmuir: *J. Am. Chem. Soc.*, 38, 2263 (1916).

⁸ Discussed in most of the previous reports of the Committee on Contact Catalysis.

⁹ First Report of the Committee on Contact Catalysis, and elsewhere.

Attention was directed in the last report¹ to three summarizing papers on this subject.² In addition to these, two recent books should be noticed. "Kinetics of Chemical Change in Gaseous Systems" by C. N. Hinshelwood (1926), although not exhaustive, is a stimulating review of the subject. It is written in such a clear fashion that the theory is within the reach of everyone. There are two chapters on heterogeneous reactions. The second book, "Statistical Mechanics with Applications to Physics and Chemistry," R. C. Tolman (1927) is more mathematical than the book by Hinshelwood. If one is not frightened off by some of the topics in the earlier chapters such as "generalized space," one finds much valuable material farther on in the book, especially with regard to photochemical reactions and certain physical questions which enter into work upon reaction velocity. Heterogeneous reactions are not discussed extensively.

The modern theory of reaction velocity is founded on the very solid ground of the molecular kinetic theory of matter. To explain the reactions whose temperature coefficients exceed the rate at which the total number of collisions increases with temperature, Arrhenius³ postulated that only certain "active" molecules enter into reaction, and that the number of these increases sufficiently rapidly with temperature to account for the observed reaction rates. It is now thought that these molecules are merely those with a sufficiently high energy content (an idea which accounts quantitatively for the experimental facts), rather than chemical isomers of the inactive molecules. Thus it would be difficult to imagine suitable isomers of hydrogen and iodine in accounting for the temperature coefficient of the combination of these two elements.

On the assumption that active molecules are merely those of sufficiently high energy content, and that every collision between active molecules led to reaction, W. C. McC. Lewis⁴ was able to calculate theoretically the rates actually observed by Bodenstein⁵ for the homogeneous formation and decomposition of hydrogen iodide.

Observed reaction rates at different temperatures are found to conform to the empirical equation⁶ $d \ln k/dT = A/RT^2$. "k" is the velocity constant, R the gas constant, T the absolute temperature, and A the heat of activation. A is constant when it is taken to be the excess energy⁷ the active molecules must have, over the average energy of all the molecules, in order for reaction to occur. From the experimental data and this equation (a straight line is obtained with slope $-A/R$ on plotting $\ln k$ against $1/T$) an "observed" value of A is obtained. From the above assumptions the number of active

¹ Reid: Fifth Report of the Committee on Contact Catalysis.

² Tolman: J. Am. Chem. Soc., 47, 1524 (1925); Lewis and Smith: 47, 1508 (1925); Hinshelwood: Chem. Rev., 3, 227 (1926).

³ Arrhenius: Z. physik. Chem., 4, 226 (1889).

⁴ J. Chem. Soc., 113, 471 (1918).

⁵ Z. physik. Chem., 29, 295 (1899).

⁶ Arrhenius: *Loc. cit.*

⁷ Tolman: "Statistical Mechanics", *loc. cit.*

molecules of hydrogen is, according to the Maxwell distribution law, equal to the total number $\times e^{-A_H/RT}$ (approx.), and the number of active molecules of iodine is equal to the total number $\times e^{-A_I/RT}$. The number of collisions between the active molecules, according to the formula given by kinetic theory, is, therefore, the total number of collisions between hydrogen and iodine molecules $\times e^{-A_H-A_I/RT} =$ the total number of collisions between molecules of hydrogen and iodine $\times e^{-A/RT}$, and by the assumptions of the theory should be equal to the observed rate of disappearance of reactants. This gives a theoretical value of A . For hydrogen iodide formation, the observed value of A is 40,000 calories per 2 gram molecules, and the calculated value is 40,200 calories, a closer agreement than could be expected, granting the correctness of the interpretation. The individual values of A_H , and A_I , representing the extents to which hydrogen and iodine must be separately activated, are not known. Indeed, it may be possible that it is immaterial how the energy of activation is distributed before collision, it merely being necessary that their joint transferable energy exceed the value A , the energy being pooled on collision. This possibility was suggested by Hinshelwood,¹ who has carried out calculations similar to the above for various reactions, which he and his students have investigated experimentally². It is to be strongly emphasized that every known uncatalyzed bimolecular reaction is interpretable quantitatively on the above lines.

| Reaction, thermal decomposition | A from collision calculation | A from temperature coefficient. | Abs. T for equal rate |
|---------------------------------------|--------------------------------------|-----------------------------------------|-----------------------------|
| 2 N ₂ O | 55,000 | 58,500 | 956 |
| 2 HI | 43,900 | 44,000 | 760 |
| 2 Cl ₂ O | 22,000 | 21,000 | 384 |

The last column gives the temperature at which the various reactions attain the same speed. Hinshelwood³ in speaking of the parallelism between the figures of the last column and the values of A says: "This is the strongest and, at the present time, the principal evidence for the reality of the energy of activation."

According to Hinshelwood,⁴ difficulties in accurately determining the heat of activation, inaccurate knowledge of the diameter of molecules, and the approximate nature of the distribution law used prevent one from deciding whether vibrational and electronic energies also contribute to the heat of activation in the above cases (only translational energy was considered in carrying out the calculations). There is some evidence⁵ that the transference of these forms of energy depends upon the specific nature of the colliding molecules.

¹ Hinshelwood and Burk: Proc. Roy. Soc., 106A, 284 (1924).

² See, e.g., Hinshelwood and Hughes: J. Chem. Soc., 125, 1891 (1924).

³ Hinshelwood: "Kinetics of Chemical Change in Gaseous Systems," p. 93.

⁴ Chem. Rev., 3, 227 (1926).

⁵ Stuart: Z. Physik, 32, 262 (1925).

Of course, if upon introducing the reactants, subsidiary quickly-established equilibria are set up, so that the concentration of a given reactant will be a different fraction of that added for different temperatures, the heat of reaction for this subsidiary reaction will be included in the measured heat of activation.¹

Dey and Dhar² propose the rule that the temperature coefficient is greater for smaller reaction orders. This cannot be an absolute rule for different reactions, for the temperature coefficients of the thermal decomposition of nitrogen pentoxide (monomolecular), and of nitrous oxide (bimolecular) contradict it.

Termolecular reactions offer no particular additional difficulties. Their general characteristics are simply interpretable in terms of the molecular kinetic theory of matter.

Unimolecular reactions, on the other hand, continue to offer grounds for controversy. The question cannot be taken up in detail here. However, Tolman's calculation³ that collision cannot activate the molecules fast enough to account for the rates of known unimolecular reactions is thought by Lewis and Smith,⁴ by Hinshelwood,⁵ and by Fowler and Rideal⁶ to offer no obstacle in case the molecules of reactant have sufficient degrees of freedom. However, Tolman, Yost, and Dickinson⁷ think that there are still difficulties with activation by collision for this type of reaction, and favor an elaborated radiation theory as most satisfactory for unimolecular reactions. It has not been made clear why both collisions and radiation cannot play a part simultaneously in such reactions.⁸ The confusion seems to arise over uncertainties regarding (1) the amount of radiation which the reactants can absorb, (2) the laws governing the transfer of internal energy at the moment of collision.

In recent experiments of Lewis and Mayer,⁹ a stream of pinene vapor was passed through a furnace under such conditions that there were no collisions, yet sufficient radiation for complete racemization. They found no racemization, and consider this to rule out radiation as the activating mechanism for this monomolecular reaction.

In the case of unimolecular reactions, the possibility was emphasized by Lindemann¹⁰ that molecules active on the energy score may have to await a suitable internal phase relationship before reaction is possible, and thus may have percentage reaction rates independent of pressure over certain ranges, even though the activation is brought about by collision.

¹ Giordani: *Rend. Accad. Sci. Napoli*, **32**, 70 (1926); *Chem. Abs.*, **21**, 3797 (1927).

² *Z. Elektrochemie*, **32**, 586 (1926).

³ *J. Am. Chem. Soc.*, **47**, 1524 (1925).

⁴ *J. Am. Chem. Soc.*, **47**, 1508 (1925).

⁵ *Proc. Roy. Soc.*, **113A**, 230 (1926).

⁶ *Proc. Roy. Soc.*, **113A**, 570 (1927).

⁷ *Proc. Nat. Acad. Sci.*, **13**, 188 (1927).

⁸ For further recent work on monomolecular reactions, see Ramsberger: *J. Am. Chem. Soc.*, **49**, 912, 1495 (1927); *Proc. Nat. Acad. Sci.*, **13**, 849 (1927); Christiansen: *Proc. Cambridge Phil. Soc.*, **23**, 438 (1926); Hibben: *Proc. Nat. Acad. Sci.*, **13**, 626 (1927); Hinshelwood and Askey: *Proc. Roy. Soc.*, **115A**, 215 (1927); **116A**, 163 (1927).

⁹ *Proc. Nat. Acad. Sci.*, **13**, 623 (1927); *J. Am. Chem. Soc.*, **49**, 3046 (1927).

¹⁰ *Trans. Faraday Soc.*, **17**, 598 (1922).

Thomson¹ now suggests a new type of internal phase relationship. He develops the view mathematically that if the intramolecular forces are intermittent, a Maxwellian distribution of energy amongst the molecules may be produced without the aid of collisions, or of the absorption and emission of radiation. He says, "The molecules with high energy will, however, not have acquired this energy by collision with other molecules but by drawing on the energy of the fields of force of the molecules." . . . "The rate of decomposition of nitrogen pentoxide depends (on this basis) on the number which attain the critical energy in unit time, rather than upon the number which have this energy when things are steady."

From the point of view of catalysis, the important points which emerge from the work on homogeneous reaction velocity are that the velocities of reactions are governed (1) by the rates at which the energy of activation can be supplied to the reactants, i.e., by the number of activated molecules per unit time (2) by a factor corresponding to the probability of reaction after activation. (2) may result from the necessity of a suitable internal phase relationship. The second factor, in the case of bi- and multimolecular reactions may depend upon a possible necessary suitable orientation as the active reactants come into the sphere of collision. This effect will not change with the temperature because an increase in the number of revolutions of the molecule per unit time will not, ordinarily, change the chance that a given orientation will occur.

According to Hinshelwood² (2) in no case can depend upon temperature. At least the variation with temperature cannot be very great—otherwise reactions would not follow the Arrhenius equation. In his work upon homogeneous reactions, Hinshelwood³ also places preponderant weight upon the first factor for reactions other than bimolecular. This view is based largely upon the approximate constancy of A/RT for reactions of a given type at temperatures of equal reaction velocity. While this is evident enough for the simple bimolecular reactions, in view of the above calculation and others like it, it is a little surprising to find this relation true for unimolecular reactions since in their case so much weight has been placed on only a few of the activated molecules reacting.⁴

In any event, the factor (2), above, would seem to have more importance in catalysis than in uncatalyzed reactions for say its whole range of influence could lead but to a factor of ten in the reaction velocity. If a catalyst could change its value from one to ten, this would be of great importance for simultaneous reactions, and in other cases, but it might not be detected for the homogeneous reactions.

According to Peacock,⁵ substitutions in certain organic molecules affect their reaction velocities much more than the corresponding heats of activation

¹ Phil. Mag., 3, 241 (1927).

² Chemical Reviews, 3, 227 (1926).

³ Chemical Reviews, 3, 227 (1926).

⁴ Lindemann: *Loc. cit.*

⁵ J. Phys. Chem., 31, 535 (1927).

for these reactions. In some cases, the reaction with the higher heat of activation had the lower rate. This would indicate considerable importance for factors other than the heat of activation. However, the heats of activation which Peacock quotes are close together and accurate measurement of them is difficult.

Although one cannot be sure that these two factors contain the whole story of homogeneous reaction velocity, yet they seem to account, at least in outline, for the observed phenomena, and give very definite factors for the catalytic investigator to keep in mind in trying to ascertain how catalysts effect the acceleration of reactions. Thus, if a catalytic agent can facilitate the energy transfer to or away from the seat of reaction, if it can reduce the amount of energy necessary for reaction, or if it can increase the probability of reaction after activation, then the phenomenon of catalysis will ensue.

As far as the writer is aware, little is known about the last factor. The possibility that the surface can cause the reactants to come into suitable juxtaposition¹ more frequently comes under this head. Oriented adsorption may aid or hinder the transfer of energy to a given part of the adsorbed molecule, or may render a given part of the adsorbed molecule more, or less susceptible to collision from the gas phase.

Facilitation of Energy Transfer

(1) *Assistance in the Dissipation of the Heat of Reaction*

According to Polanyi and Herzfeld² and to Born and Franck³ certain exothermic reactions of the type $A + B = C$ cannot take place unless there is a third molecule present to carry off the heat of reaction, the system being unable to radiate it. This is one way in which a catalyst might assist certain reactions.

The reaction of dried ammonia with dried hydrochloric acid is visibly heterogeneous.⁴ The effect of the glass walls here might be due to their assistance in the dissipation of the heat of reaction. This mechanism might also explain the effect of metals in catalyzing the recombination of hydrogen atoms,⁵ which has been applied by Langmuir⁶ in an ingenious fashion to the welding of metals.

Facilitation of Energy Transfer to the Reacting Molecules

The Lewis-Perrin theory of catalysis⁷ would come under this head. Although this theory offers no hope of explaining catalysis in general, no grounds exist for ruling it out completely. Catalysis by photosensitized mercury atoms, which is being actively investigated at the present time,⁸ is

¹ Langmuir: *Trans. Faraday Soc.*, 17, 618 (1922).

² *Z. Physik*, 8, 132 (1922).

³ *Ann. Physik*, (4) 76, 225 (1925).

⁴ Burk: *Dissertation*, Oxford (1926).

⁵ Wood: *Proc. Roy. Soc.*, 102A, 1 (1922).

⁶ *Ind. Eng. Chem.*, 19, 6 (1927).

⁷ See the First Report of the Committee on Contact Catalysis for references. Also Perrin: *Trans. Faraday Soc.*, 17, 566 (1922).

⁸ Taylor and Bates (summarizing paper): *Proc. Nat. Acad. Sci.*, 12, 714 (1926).

closely related to the mechanism proposed by Lewis and Perrin for the action of surfaces.

The homogeneous thermal decomposition of nitrous oxide¹ requires a heat of activation of about 58,000 calories per two gram molecules, and is bimolecular. The heat of activation of the heterogeneous decomposition on gold² is about the same per molecule, but the reaction is unimolecular, collision between active molecules being unnecessary. Here the increase in rate results from the kinetic simplification.

Hinshelwood³ presents the following picture which is a possible factor in catalysis and comes under this head. "We may suppose a molecule to be composed of two parts, A and B, the separation of which constitutes the chemical decomposition of the molecule. Let B receive an impact from another molecule, which imparts to it momentum directed away from A. The small inertia of A enables it to follow B without the development of much strain between them. If, however, A were firmly enough held to a surface, its inertia might be so great that the accelerating force instead of drawing A after B would cause the disruption of the bond between them."

Lowering of the Heat of Activation

The great importance of the energy of activation in homogeneous reaction velocity has already been emphasized. It is reasonable to expect the energy of activation to play a correspondingly important rôle in heterogeneous reactions, since the two types cannot be fundamentally different.

In some heterogeneous reactions, e.g., the catalytic thermal decomposition of ammonia upon a tungsten surface⁴ the other factors seem to drop out. At 100 mms. pressure, the reaction is experimentally of zero order, and therefore cannot depend upon collisions from the gas phase. Other experiments show that the reaction is really monomolecular and, therefore, cannot depend upon a suitable orientation of colliding molecules of ammonia upon the surface. The photochemical decomposition of ammonia requires ultraviolet light, and it is most unlikely that the tungsten can give rise to the necessary increase in density of this radiation under the conditions of thermal decomposition. For such a simple molecule, judging from the behavior of other simple molecules in the bimolecular reactions already discussed, the probability of reaction after activation must be high. The reaction is unretarded by products, and since the reaction is zero order (i.e., the active surface is practically completely covered with ammonia), the observed heat of activation, 38,700 calories per gram molecule, is the true heat of activation. The heat of activation for the homogeneous bi-molecular change must be greater than 80,000 calories per gram molecule, since this reaction is not perceptible at 1000 degrees centigrade. The homogeneous unimolecular re-

¹ Hinshelwood and Burk: Proc. Roy. Soc., 106A, 284 (1924).

² Hinshelwood and Pritchard: Proc. Roy. Soc., 108A, 211 (1925).

³ "Kinetics of Chemical Change in Gaseous Systems," p. 197.

⁴ Hinshelwood and Burk: J. Chem. Soc., 127, 1105 (1925).

action would probably have a higher heat of activation still, and it is this reaction with which the unimolecular heterogeneous reaction should be compared. There seems to be little doubt that in this reaction the catalyst has effected a large reduction in the heat of activation. There is also little doubt that catalysts often do this.

Euler and Olander¹ find that the temperature coefficient for the enzymatic inversion of cane sugar is smaller than without the enzyme. Many other examples could be quoted.

How can the catalyst lower the heat of activation of the reactants by adsorbing them? That it must "distort," "dislocate," "strain," or "profoundly modify" the adsorbed molecule in some way seems to be an opinion widely held.² But these terms are too indefinite to serve as a guide in prescribing catalysts for given purposes.

Two rather definite ways have been suggested in which bonds in the adsorbed molecules can be loosened, or opened up, and the energy of activation thus lowered for the breaking of that bond.

1. *Atomic distortion theory.*

The older picture³ is, quoting Langmuir: "In view of the structure of atoms from positive and negative particles, it is clear that the atoms should have the properties of a dielectric. Thus, if we had a chain of atoms held together by duplets—as, for example, in the hydrocarbon chain of an organic compound—and we bring a positively charged body near one end of the chain, the electrons will be attracted and the nuclei repelled, so that a certain displacement of these particles with respect to one another will result. This effect is then transmitted with gradually decreasing intensity from atom to atom throughout the length of the chain. The chemical evidence indicates clearly that effects of this kind are transmitted relatively great distances . . . In cases where atoms are not joined together by duplets, we should never expect the transmission of electric force to extend through more than about one atom." On page 616 of the same paper we find, "when gas molecules condense on a solid surface in such a way that they are held on the surface by primary valence forces involving a rearrangement of their electrons, their chemical properties become completely modified. It is not surprising, therefore, that in some cases such adsorbed films should be extremely reactive, while in other cases they may be very inert to outside influences."

Presumably, some such idea is behind the speculations of Flürscheim,⁴ who postulates, if the writer understands him, that, if different atoms are attached to a foundation atom, the greater the strength of attachment of one atom the smaller is the remaining available total valence force of the foundation atom, for other atoms.

¹ *Z. anorg. allgem. Chem.*, 156, 143 (1926).

² Böseken: *Rec. Trav. chim.*, 29, 85 (1910); 30, 381 (1911); 39, 623 (1920); 46, 458 (1926); Raschig: *Z. angew. Chem.*, 19, 1748, 2083 (1906); Bodenstein: *Ann.*, 440, 177 (1924); Zelinski: *Ber.*, 58, 2755 (1925); Hinshelwood: "Kinetics of Chemical Change in Gaseous Systems," p. 188.

³ Graham: *Proc. Roy. Soc.*, 16, 422 (1868); Langmuir: *Trans. Faraday Soc.*, 17, 610 (1922).

⁴ *Chem. and Ind.*, 3, 246 (1925) (summarizing paper).

Possibly some such idea as that sketched above is back of the suggestion of Taylor¹ that the action of oxides in accelerating both the dehydration and dehydrogenation of formic acid, though metals accelerate "only" the dehydrogenation,² is due to the presence of both positive and negative ions in the oxide. In this connection, it is not obvious why the electrons in the metal cannot induce dehydration as well as the negative ions of the oxide, if the charge is the important thing. On the basis of Taylor's idea, a stream of electrons, however slow, should be able to dehydrate formic acid, and should have general catalytic action. No experiments were available to the writer on this point.

In connection with this atomic distortion theory of surface action, it is to be remarked that if the electrical forces of the catalyst actually do seriously distort the electronic orbits in the atom or atoms adjacent to the catalyst, in some cases it seems possible that this would have no effect upon the succeeding bond; in other cases it might strengthen the succeeding bond, and in still other cases weaken it. These possibilities correspond to the three cases cited by Franck,³ in which bonds can be weakened, strengthened, or unaffected by electronic excitation in the constituent atoms.

From the work of Birge and Spomer,⁴ and Birge,⁵ it seems that, according to the quantum interpretation of band spectra, the energy necessary for the dissociation of an excited molecule is sometimes about the same as that for the unexcited molecules.

Further evidence that possible electronic disturbance does not greatly affect certain bonds is the persistence of the positions of certain infra-red spectra, and the characteristics of certain ultra-violet spectra which are traceable to certain bonds, for instance, C - H, C - C, O - H, and N - H, in various compounds⁶ in which different substituents are attached to the atoms constituting the bond in question.

On the other hand, Ephraim and Block⁷ found that in the reflection spectra of the series of ammonates of PrCl₃, there were shifts in the positions

¹ "Colloid Symposium Monographs," 4, 19 (1926).

² This does not exactly represent the accurate facts. There is some dehydration on silver, for example, at 185°. (Hinshelwood and Tingey: *J. Chem. Soc.*, 121, 1668 (1922)). At 355°, tinned iron gives mostly carbon dioxide and hydrogen; but at 255°, the same catalyst gives also carbon monoxide. (Tropsch: *Abhandl. Kenntnis Kohle*, 7, 1 (1925)); *Chem. Abs.*, 21, 3530 (1927). The remarkable instance is given by Sabatier ("Catalysis in Organic Chemistry", p. 76) where finely divided chromium oxide decomposes ethyl alcohol giving a gas containing 91% ethylene (dehydration). The crystallized oxide is not so active, and at higher temperatures causes dehydrogenation almost exclusively. As Professor Taylor has reminded me, films of oxide may bring these results on silver and tin into line; but films may also jeopardize the conclusions on the pure metals.

³ Discussion of the Faraday Society on Photochemistry, 536 (1925).

⁴ *Phys. Rev.*, (2) 28, 259 (1926).

⁵ "Molecular Spectra in Gases," *Nat. Res. Council Bull.*, No. 57 (1926).

⁶ Coblenz: *Investigations of Infra-Red Spectra*, Carnegie Inst. Pub. (1905-1908); *Le Compt. Rend.*, 178, 1530, 1698, 2073 (1924); Marton: *Z. physik. Chem.*, 117 97 (1925); Ellis: *J. Optical Soc. America*, 8, 1 (1924); *Phys. Rev.* (2) 23, 48 (1924); 27, 298 (1926); 28, 25 (1926); *Proc. Nat. Acad. Sci.*, 13, 202 (1927); Bell: *J. Am. Chem. Soc.*, 97, 2192, 3039 (1925); 48, 813 (1928); Bonino: *Chem. Abs.*, 20, 709, 710, 2950 (1926); Henri: "Structures des Molécules" (1925); Morton and Riding: *Proc. Roy. Soc.*, 113A, 717 (1926).

⁷ *Ber.*, 59, 2692 (1926).

of the spectra toward the ultra-violet, which they attribute to compression of the electron shells. However, according to Biltz,¹ the molecular volume of ammonia in ammonates is very close to the value in the gas phase.

In this same connection, according to Schaefer and Schubert² the inner vibration frequencies of ions (e.g., nitrate, sulphate, and carbonate ions), are independent of the nature of the metal ion and therefore of large differences in electric field strength, (arising from differences in screening constants of the positive ions in the case of ions of the same apparent charge). According to Taylor and Rideal,³ the characteristic frequencies of vibration of sulphur are almost the same in all the phases.

Bowen⁴ has pointed out the constancy of heats of linkage in various compounds.

The writer⁵ has recently carried out the thermal decomposition of ammonia upon fine electrically heated wires, in the presence of electric field strengths as high as 140,000 volts per cm. This field is as strong as those used in investigations of the Stark effect and therefore produces some distortion of the electronic orbits. No effect was observed upon the rate of decomposition of the ammonia. The experiments, however, are not considered to be conclusive against the atomic distortion mechanism for lowering the energy of activation.

The rate of decomposition of nitrogen pentoxide is about the same in a solution of chloroform as in the gas phase,⁶ yet chloroform has a very considerable electric moment.⁷ This is strong evidence that the electric fields of chloroform do not affect the bonds of nitrogen pentoxide. Similarly, Smith⁸ has found that the rate of the unimolecular racemization of pinene in solution in petroleum, acetophenone, and alpha methyl naphthalene is nearly the same as that in the pure liquid, and in the gas phases.

On the theoretical side, Kemble⁹ has pointed out that one of the characteristics of the quantum behavior of atoms, is the way in which electrons in orbits ignore forces which, on the basis of classical mechanics, would cause a profound change in their path. He points out that the electronic orbits must be essentially preserved upon collision, etc., if this is not too violent, and also points out the similarity of situation of atoms in collision and in compounds. Thus it may turn out that the quantum laws will rule out the atomic distortion mechanism for the lowering of the energy of activation by catalysts, at least in some cases. It is to be remembered in this connection that catalysts have to deal with molecules, in which loosely attached, or transferable electrons have had the opportunity of taking up positions of relatively greater stability than in the case of the free atoms.

¹ Z. anorg. allgem. Chem., 159, 96 (1926).

² Ann. Physik, (4) 50, 283 (1916); 55, 577 (1918).

³ Proc. Roy. Soc., 115A, 598 (1927).

⁴ Discussion of the Faraday Society on Photochemistry, 544 (1925).

⁵ Proc. Nat. Acad. Sci., 13, 719 (1927).

⁶ Lueck: J. Am. Chem. Soc., 44, 757 (1922).

⁷ Henri: "Structure des Molécules," *loc. cit.*

⁸ J. Am. Chem. Soc., 49, 43 (1927).

⁹ Kemble: In "Molecular Spectra in Gases," Nat. Res. Council Bull., No. 57 (1926).

However, the work of Born¹ and others seems to give considerable importance to the deformation of ions and atoms, in accounting for chemical bonds.

One would expect the atomic distortion, or electronic orbit distortion effect, to influence all the chemical bonds within the range of its action.² This is not very well in line with the extreme specificity of some catalysts. One of the things catalytic chemists must explain some day is the ability of enzymes to accelerate exclusively one reaction with a large delicate organic molecule capable of many reactions. Atomic distortion, carried through the chain, does not seem to the writer to be a very promising approach to this problem.

With regard to the chemical evidence for such effects, it is not obvious that the results of organic chemistry, such as the effect upon the strength of an acid of substituents in the chain, should point unequivocally to atomic distortions. Such substitutions could affect the degree of association of the organic molecules, could affect the spatial position of the atoms in the molecule with respect to each other,³ etc., without affecting the individual bonds.

Finally, with regard to the atomic distortion, or electronic orbit distortion theory for the lowering of the energy of activation by catalysts, we may conclude that it has not been shown definitely to be impossible in any case, although in some instances there is considerable evidence that it is inoperative. Although the theory is old enough, it has never enabled one to prescribe a catalyst for a given purpose—which is not what one would expect of a correct theory of phenomena in which such wide interest has been shown as in catalysis. Nevertheless, the work of Born and others compels one to give the theory serious consideration.

One knows that in some reactions there is a complete transference of one or more electrons. Presumably, however, such processes take place in accordance with quantum laws. The all-important point then is: If an external force is not sufficient to effect a complete quantum change, does it, nevertheless, distort the arrangement of the electronic orbits seriously or not? If it does distort them seriously, what part does this distortion play in catalysis?

Molecular Distortion Theory

There is another way in which adsorptive forces can lower the energy of activation, namely by actually partially separating the atoms forming the bond which is to be broken. A consideration of the extremely short range of chemical forces led Langmuir⁴ to the extremely fruitful, and now generally accepted, theory of monomolecular adsorbed gas films on solids. A consideration of the same thing, namely the short range of chemical forces, led

¹ Z. Elektrochemie, 30, 382 (1924) (summarizing paper). See the discussion of "bonds" later in this report. Fajans and Joos: Z. Physik, 23, 1 (1924).

² According to Langmuir (*loc. cit.*) the effect can be carried relatively long distances through a chain of atoms.

³ By an effect which could be pictured as being similar to the opening or closing of a hinge by forces (due to the substituent in the case of the organic molecules).

⁴ J. Am. Chem. Soc., 38, 2252 (1916); Trans. Faraday Soc., 17, 610 (1922).

the writer¹ to the theory that the forces of adsorption (apart from the atomic distortion effect discussed above) can separate the atoms forming a bond only if the molecule is multiply adsorbed on the surface, i.e., adsorbed at more than one point by more than one atom of the catalyst. The catalytic effect of the surface clearly would then depend upon the spacing of the adsorbing points in the surface, which spacing would have an optimum value for a given reactant. The catalytic effectiveness of the surface would also depend upon the specific attraction of the adsorbing atoms of the surface for the atoms of the adsorbed molecule by which it is, in the main, attached to the surface.

That a gas could be attached to a surface by more than one point seemed the best explanation for observations of Hinshelwood and Burk² that added hydrogen sometimes failed to poison a quartz surface for the thermal decomposition of ammonia. A similar situation exists in the case of the poisoning action of carbon monoxide for its oxidation at a quartz surface.³

A rather striking result of Tropsch and von Philippovich⁴ should be mentioned in this connection. They found that the catalytic activity of nickel in decomposing carbon monoxide was almost completely destroyed by alloying the nickel with fifty percent tin. The possibility at once suggests itself that isolated nickel atoms, and tin-nickel pairs cannot effect the decomposition, and that suitable nickel-nickel spacings in the alloyed catalyst are infrequent.

The multiple adsorption theory is mechanically possible, and catalytic action must follow from it necessarily. If conditions (spacing, etc.) are right, it must exist, independent of the existence of the atomic distortion mechanism. It is therefore a mechanism which should be kept in mind when considering any case of catalysis. In the case of symmetrical molecules such as H₂, N₂, O₂, etc., why should one atom be attached to the surface in preference to the other? Similarly, why should not straight chain hydrocarbons, dibasic acids, and a great many other substances lie flat upon the surface? According to good evidence of Palmer and Constable⁵ for the case of alcohols adsorbed on copper, the molecules are attached to the copper by the alcohol group. The entire CH₂OH group cannot possibly lie over a single copper atom, and if it does not, then the *localized* forces of the other copper atoms cannot avoid stretching the alcohol group in the way sketched above.

None of the points mentioned at the beginning of this report is in contradiction to this theory. Promoter action, and the specificity of catalysis, even to the extreme found in enzyme action, become particularly clear on this basis.

¹ J. Phys. Chem., 30, 1134 (1926).

² J. Chem. Soc., 127, 1105 (1925).

³ Bodenstein and Ohlmer: Z. physik. Chem., 53, 166 (1905); Benton and Williams: J. Phys. Chem., 30, 1487 (1926).

⁴ Abhandl. Kenntnis Kohle, 7, 44 (1925); Chem. Abs., 21, 3530 (1927).

⁵ Proc. Roy. Soc., 107A, 255 (1925).

The Nature of Chemical Bonds

If we are to come to a sound decision regarding the effect of the catalyst upon chemical bonds, it seems necessary to discuss the question of the nature of such bonds. A short summary will therefore be given of recent efforts toward the solution of that problem.¹

Starting with the universally accepted premise that matter is composed of positive and negative charges of electricity, that these are in motion, and that they have mass, it would seem that gravitational, magnetic, and electrostatic forces should be taken into consideration in an examination of the question of the nature of chemical bonds. There is no need to assume a special "chemical" force until the three ordinary types of physical force can be shown to be incompetent of explaining chemical combination. This problem presents, perhaps the most urgent immediate need for co-operation between chemists and physicists.

According to Herzfeld² one can immediately neglect gravitational and magnetic forces. He says "concerning the nature of the fields (around atoms) only electrostatic actions need be considered. All other forces (electromagnetic or gravitational) are too weak: there are no grounds for assuming an unknown force."

Kemble³ says: "Calculations by Mensing seem to indicate that magnetic forces between magnetic atoms are not strong enough to play an important part in molecular formation."

Such statements come as something of a shock to chemists who have been under the influence of the Lewis-Langmuir theory of valence. Lewis⁴ says: ". . . the pairing of electrons, which I have regarded as the most fundamental phenomenon in all chemistry is some sort of conjugation of two magnetons of such a character as to eliminate their magnetic moment." He also says, p. 147, "In previous chapters it has occasionally been hinted that in place of the electric it is the magnetic properties of the atom and the molecule which determine their essential structure. In the present chapter, we shall give free rein to this idea."

¹ Since completing the manuscript of this report, a copy of N. V. Sidgwick's new book, "The Electronic Theory of Valency" (1927), has come into the writer's hands. He strikes an admirable note in the preface, where he says, "In developing the theory of valency there are two courses open to the chemist. He may use symbols with no definite connotation . . . or he may adopt the concepts of atomic physics—electrons, nuclei, and orbits—and try to explain the chemical facts in terms of these. But if he takes the latter course, as is done in this book, he must accept the physical conclusions in full, and must not assign to these entities properties which the physicist has found them not to possess. He must not use the terminology of physics unless he is prepared to recognize its laws."

However, a rather superficial examination of the book (in the short time available) does not show that Sidgwick has emphasized the points about valence which, from the point of view of catalysis, must be brought out. One must know something of the actual nature of the binding forces, the law according to which they vary with distance, and under what conditions, and to what extent they can be affected by other forces.

² Geiger and Scheel's "Handbuch der Physik", 22, 392 (1926).

³ In "Molecular Spectra in Gases," Nat. Res. Council Bull. No. 57 (1926).

⁴ "Valence and the Structure of Atoms and Molecules," p. 148 (1923).

Williams,¹ Shaffer and Taylor,² and Taylor,³ find molecules with an odd number of electrons to be paramagnetic and those with an even number diamagnetic, which they suggest to be evidence for magnetic valence forces. Shaffer and Taylor find that complex ion formation with paramagnetic ions reduces the susceptibility of these ions and say: "We must conclude from this that chemical bonds are partly or wholly magnetic in character, or that they are formed by the same electrons which give rise to the magnetic properties." Although the latter conclusion is preferable to the former, neither seems inevitable.

It seems that gravitational forces are more insignificant than magnetic forces, as compared to the electrostatic forces available around atoms.

If then, gravitational and magnetic forces are really unimportant, it throws the whole burden of chemical valence upon electrostatic forces. The use of purely electrostatic forces in holding the simple extremely polar molecules (like sodium chloride) together needs no defense from the point of view of either the chemist or the physicist; but such bonds are the least interesting from the point of view of catalysis.

While non-polar bonds have not been worked out to one's complete satisfaction, their general features seem to be in line with the possibilities of the purely electrostatic theory. The striking characteristics of such a bond are: (1) constituent atoms are themselves electrically neutral, (2) the non-polar forces are extremely specific, (3) they fall off not in accordance with the inverse square of the distance, but with a power usually much higher than the second.⁴

If the charges in an atom are not symmetrically distributed (the negative charges around the nucleus,) the electrically neutral atom will have a resultant electrical moment; it will be a dipole. If the center of gravity of the positive charges in the atom coincides with the center of gravity of the negative charges, there can still exist a pole of higher order (in case all points in a spherical shell around the nucleus are not at the same potential, which seems to be the case in atoms). Now dipoles and the poles of higher order attract one another. The following table⁵ gives the inverse power of the distance according to which the potential energy between two poles of the order indicated varies with distance.

| | Dipole | Quadrupole | Tetrahedral Pole | Cube Pole |
|------------|--------|------------|------------------|-----------|
| Pole | 2 | 3 | 4 | 5 |
| Dipole | 3 | 4 | 5 | 6 |
| Quadrupole | | 5 | 6 | 7 |
| Cube pole | | | | 9 |

¹ Phys. Rev., (2) 23, 167 (1926).

² J. Am. Chem. Soc., 48, 843 (1926).

³ J. Am. Chem. Soc., 48, 854 (1926).

⁴ Langmuir: J. Am. Chem. Soc., 38, 1852 (1917).

⁵ Herzfeld: Geiger and Scheel's "Handbuch der Physik," 22, 440 (1926).

The values given in the table cover the range estimated from experiments with actual atoms and listed above as one of the characteristics of non-polar valence forces. The pole orders are all possible ones on the basis of the Bohr theory of the atom. If the electric charges are in motion, the pole orders are said to be increased¹ somewhat.

The possibility exists that there must be a synchronization of electronic periods in the two relevant atoms for firm binding.²

These considerations would lead one to expect forces with physical characteristics similar to the ones coming into play in non-polar unions around all atoms whose structure is according to the Bohr theory. For atoms of greatest symmetry (the rare gases) the pole order would be highest, the cohesive force would fall off with a very high power of the distance, and the energy necessary to overcome the cohesive forces $\int_{r_0}^{\infty} f(r)dr$ would be small. $f(r)$ is the force; r is the nuclear separation; r_0 is the equilibrium value of r without external forces. So far so good.

But things are not so simple as this. The carbon atom has high symmetry, but the energy necessary to separate two carbon atoms is great. On the other hand, the energy necessary to separate two helium atoms is small, whereas the pole order cannot be very great (if the nucleus is considered as a point charge).

A consideration of the preceding table gives a fair general picture of the way non-polar forces can be specific. If the synchronization factor, mentioned above, is real, it would of course involve specificity of the highest degree.

Debye³ has sought to account for van der Waals forces through mutual induced polarization of the atoms. (The fields due to the permanent poles would cancel out at large distances for rotating molecules).

Born⁴ has calculated the magnitude of induced polarization in the case of the ions of sodium chloride and other molecules, and considers the effect of great importance in chemistry. He says, "The principal result of the investigations is that, energetically at least, there is no place for directed valences, in the ordinary sense of the word, in the cases considered." It would seem that induced polarization would be of greatest importance when an ion is in the immediate neighborhood of an easily deformed atom or ion; but that the very strong bonds between carbon atoms, for instance, should be due to any marked extent to the mutual deformation of the respective atoms seems rather unlikely.

Palmer⁵ has continued his work on the critical voltages necessary to make a current flow through a coherer, when different gases are present. He appears to consider his results to be a verification of the dipole theory of adsorption. Whatever can be said for the theory, the experimental "test" of it led to

¹ Hersfeld: *Loc. cit.*

² Kemble: *Loc. cit.*

³ *Physik. Z.*, 21, 178 (1920).

⁴ *Z. Elektrochemie*, 30, 385 (1924) (summarizing paper).

⁵ *Proc. Roy. Soc.*, 110A, 133 (1926).

results in contradiction to those obtained in other ways; for instance, the heat of adsorption of hydrogen on tungsten was found to be greater than that of hydrogen on platinum, and both much greater than the other results would lead one to expect.

The possibility of an electron executing an orbit belonging to two nuclei is the next to be considered. This corresponds to the concept of the sharing of electrons, which has been found to be convenient in working out "octets", etc. It is desirable to make this idea as definite as possible, for in so far as the nucleus of one atom exerts some attractive force upon all of the electrons of an adjacent atom, all of the electrons are shared.¹ The idea of shared electrons, or binuclear orbits, does not seem to be in such great favor with those who have tried to work out the dynamic models in the simple cases.²

Kemble makes the following statement. "Any explanation of the attractive force between the atoms in a non-polar molecule consistent with the possibility of an adiabatic dissociation into normal atoms must depend upon the electric field due to the polarization of the atoms, whether that polarization be of the simple dipole type or of the quadrupole type." (Such dissociation is apparently indicated by certain work on band spectra). This does not leave much room for shared electrons, if the statement is right.

On the other hand, according to Mulliken,³ the multiplicity of the electronic levels revealed in the band spectra of certain molecules is of the same type as for the line spectra schemes for atoms with the same number of external electrons; for instance, CN is compared with sodium. This would indicate a rather aggravated case of the sharing of electrons. It would seem difficult to extend the idea, e.g., to cane sugar.

It has been proposed that in certain instances, groups containing a number of electrons different from eight are stable. Thus, Stoner⁴ proposes ten in some instances. Grimm and Sommerfeld⁵ suggest four in some cases; Niven⁶ allows six, etc.⁷

Because some molecules have been found to possess a considerable electric moment, there has been a tendency to consider the links as ionic, in disregard of chemical evidence. Thus, Hund⁸ has considered the ammonia molecule to contain the ion N^{--} and three H^+ ions. Van Arkel and de Boer⁹ consider methane to contain the ion C^{+++} and four H^- ions. If these structures represent the facts, the chemist would like an explanation of their chemical behavior.

¹ Sidgwick ("The Electronic Theory of Valency") discusses such orbits.

² See Kemble: *Loc. cit.*

³ *Phys. Rev.*, (2) 26, 561 (1925), and elsewhere.

⁴ *Phil. Mag.*, 3, 336 (1927).

⁵ *Z. Physik*, 36, 36 (1926).

⁶ *Phil. Mag.*, 3, 1314 (1927).

⁷ Sidgwick, "Electronic Theory of Valency," p. 62.

⁸ *Z. Physik*, 32, 1 (1925).

⁹ *Z. Physik*, 41, 27 (1927).

It is of great importance whether a link is ionic or not, and if only partially so, to what extent it is ionic. Thus Grimm and Sommerfeld¹ present evidence that the ions in boron nitride are B^- and N^+ and not B^{+++} and N^{---} as one might expect if the electrons transferred in such a way as to complete their octets. If catalysts act, in part, through disturbance of electrons by electrical forces, boron nitride might be expected to be a sensational catalyst, on the basis of $B^{+++}N^{---}$, but not as B^-N^+ .

Franck, Kuhn, and Rollefson,² and Franck and Kuhn³ seem to have developed a reliable method for distinguishing between ionic and non-ionic links, if their interpretation is correct. According to them, a purely polar diatomic molecule can be dissociated photochemically in one elementary act into either normal atoms, or a normal and an excited atom, whereas non-polar or semi-polar molecules, on dissociation in a similar way, cannot give two normal atoms.

Apparently, rules governing the formation of ions cannot be laid down from the ionization potential data. Noyes and Beckman⁴ say, "In general, energies of removal of the successive electrons seem to play a secondary part in determining the valencies that exist." However, Rolla and Picardi⁵ trace certain relations, not altogether new, between chemical properties and ionization potentials. Ions like Al^{+++} would seem very unlikely on the grounds of the energy necessary to remove the electrons, yet the chemical evidence for their existence is hard to get around. One would like to know why Coulomb's law should be brilliantly confirmed in Bohr's theory of the hydrogen atom, and disregarded in favor of certain alleged stable arrangements of electrons when it comes to the matter of the formation of ions.⁶

Chemists apparently now recognize polar, non-polar, hemi-polar⁷ and coordinated links.⁸ Sidgwick shows that the electron pair interpretation of the coordinate link results in an electric moment and is therefore inclined to identify the coordinate and hemi-polar links. There are, however, cases of molecules without coordinate or polar links which have marked electric moments (ammonia), in which case perhaps the idea of a hemi-polar link may apply.

Investigations of band spectra are yielding some of the most direct and definite information regarding the nature of bonds, and may offer the best

¹ *Loc. cit.*

² *Z. Physik*, 43, 155 (1927).

³ *Z. Physik*, 43, 164 (1927).

⁴ *Proc. Nat. Acad. Sci.*, December (1927).

⁵ *Chimie et Industrie*, 16, 531 (1926).

⁶ No attempt will be made in this report to discuss valence or any of the problems connected with catalysis in terms of the new quantum mechanics. It is too difficult to get physical concepts from the new mechanics, and there is no indication that the problem of valence will receive an early satisfactory solution from this quarter. See, however, Heitler and London: *Z. Physik*, 44, 455; Sugiura: 45, 484 (1927).

⁷ For recent work see Perrin: *Compt. rend.*, 185, 557 (1927); Noyes: *Cohen Festschrift*, *Z. Physik. Chem.*, 130, 323 (1927); Lux: *Z. physik. Chem.*, 121, 456 (1926).

⁸ Sidgwick: *Chem. and Ind.*, 46, 799 (1927); "Electronic Theory of Valency," (1927); Lessheim, Meyer, and Samuel: *Z. anorg. allgem. Chem.*, 165, 253 (1927).

way of finding out to what extent a bond is changed by outside influences, such as the fields of other molecules, or ions, substituents, etc. Some of this work has been previously discussed.

Mecke¹ has attempted to correlate band spectra of various diatomic molecules and the periodic system of the elements. He calculated the binding forces in the various compounds using the potential law $P = - [c_1/r^p - c_2/r^q]$, c_1/r^p taking into account the attractive force and c_2/r^q the repulsive force. All the constants are spectroscopically accessible. Of the compounds examined, he concluded that the hydrides could be considered as polar since $p = 1$ (Coulomb's law). The remaining compounds he examined appeared not to be polar since p was found to be three or four, and q six to ten.

In addition to the work previously referred to regarding the influence upon bonds of substitution, etc., the following results have been obtained.

Bovis² has found that the absorption spectra of bromine in water, carbon tetrachloride, chloroform, ethyl alcohol, and carbon disulphide consist in all cases of two absorption maxima, one of which lies in the violet at approximate wave-length 0.410μ and the other in the ultra-violet at approximate wave-length 0.260μ . The widths of the bands were unchanged from one solution to another.

Scheibe, Felger, and Rossler³ show that the shifts in the wave-length of ultra-violet light absorption and changes in the amount of light of this wave-length absorbed when the same substance is dissolved in various solvents are two quite different phenomena. They attribute the first to solvation at the active bond, and support this by cryoscopic measurements. The authors realize that in the spectral shifts one has a tool for getting at the molecular deformation necessary to explain catalysis, although they did not determine just what the deformations were in the cases studied.

It is unfortunate that none of the work which the writer has been able to find upon band spectra enables one to decide whether substitution, solvent forces, etc., definitely alter bonds or not. In some of the papers the position of a band attributed to a given link seems to persist practically unchanged from compound to compound, and from solvent to solvent. In other cases, there seems to be an appreciable, though usually small, shift, but it has not been traced definitely to a change in the binding force. The position and characteristics of a band, due to vibrations (\pm rotations) of a given link will, according to the quantum interpretation, depend not only upon the binding force and the law according to which it varies with distance, but upon the mass of the vibrating atoms. From the point of view of catalysis, what one would like to see brought out is the effect of substitution, etc., upon the strength of binding, distinct from any effect due to change in mass.

¹ *Z. Physik*, 42, 390 (1927).

² *Compt. rend.*, 185, 57 (1927).

³ *Ber.*, 60, 1406 (1927).

Condition of Adsorbed Gases

It is thinkable that adsorbed gases can be essentially unchanged, can be stretched, can be resolved into atoms, can have their electronic orbits distorted, can be ionized, etc. Some of these possibilities have already been discussed.

Resolution into Atoms.—H. S. Taylor¹ proposes resolution into atoms as the mechanism of activation for diatomic gases, e.g., hydrogen. It seems, however, to the writer that atomic hydrogen would probably be less active upon the surface than stretched molecules, because the bond catalyst-hydrogen atom would be stronger than the catalyst — H — H bond and would itself require activation in order that the atomic hydrogen become reactive. According to this view, there would be an optimum degree of stretching which would give more active hydrogen than resolution into atoms.

Kistiakowsky² has continued the Princeton work on the investigation of the condition of adsorbed gases on metal surfaces by the method of electronic impact. He felt confident that there is atomic nitrogen on the surfaces, but was not certain with regard to the hydrogen. If his conclusions are correct, it does not follow, however, that all the nitrogen on the surface is atomic, nor that the atomic nitrogen is the most reactive.

Ions on the Surface.—The view is held in some quarters³ that the function of the catalyst is to ionize the adsorbed gases. The writer does not follow the argument that adsorption should necessarily lead to ionization, and can see no need for the assumption of ions as a preliminary state for chemical reactions in general.

Dhar⁴ thinks reactions are hastened by the presence of ions. He considers these to combine with the reactants forming a more reactive complex. He proposes that heterogeneous catalysis is due to dissociation of the adsorbed gas into ions and electrons which then activate other molecules of adsorbed gas and induce the desired reaction. This is not impossible, as far as one can see, but neither does it seem likely as a general explanation of catalysis, for many catalytic reactions take place under conditions where ionization would seem most unlikely.

In this connection, Hutchison and Hinshelwood⁵ find that the relative difficulty of decomposing ammonia and nitrous oxide by molecular collision is maintained (roughly) when the collision is with ions.

Pisarzhevskii⁶ thinks that in the catalytic decomposition of potassium chlorate by metals and oxides, the electrons of the catalyst ionize the adsorbed gases by their impacts. On leaving the catalyst, he thinks the gaseous

¹ Proc. Roy. Soc., 113A, 77 (1927).

² J. Phys. Chem., 30, 1356 (1926).

³ Bone: Proc. Roy. Soc., 112A, 477 (1926); Brewer: Phys. Rev. (2) 26, 633 (1925); Proc. Nat. Acad. Sci., 12, 560 (1926).

⁴ Z. anorg. allgem. Chem., 159, 103 (1926).

⁵ Proc. Roy. Soc., 117A, 131 (1927).

⁶ Chem. Abs., 21, 2415 (1927).

ions act on the molecules of the chlorate and bring about a series of electronic transferences resulting in the decomposition of the chlorate molecule.

Gray¹ suggests that clouds of electrons in the immediate vicinity of the surface are the active influence in promoting vigorous reactions at surfaces.

Bone² examined the influence of drying upon the catalytic combustion of carbon monoxide over oxides and metals. The immediate effect of drying was always to increase the apparent catalytic power of the surface, and the ultimate effect to diminish or completely stop the catalytic combustion. It is difficult to see how he concludes that these results would be best explained if the prime function of the catalyst surface is to ionize the reacting gases.

These authors have not been very definite as to how they considered ionization of the reactants to explain catalysis. Also, their experiments, so far as the writer can see, have not demanded the ionization explanation. Nevertheless, there is considerable evidence for electrical effects accompanying adsorption in some cases.

Finch and Stimson³ have examined the charging of gold and silver surfaces when heated in the presence of various gases, and in vacuo. They conclude, (1) that the charge on hot gold or silver surfaces in contact with gases is due to an activation of the gas whereby its molecules become electrically charged, (2) that the activation of a compound molecule such as water-vapor or carbon dioxide involves at least its dissociation.

These conclusions can be true if the definition of activated molecules is different from that used for purposes of reaction velocity, and there is nothing in the experiments to show that all molecules chemically active have been activated in such a way as to involve electrical charging or complete dissociation.

Brewer⁴ has found that the heterogeneous oxidation of xylene, toluene, benzene, ethyl alcohol, etc., produced currents of 1×10^{-16} amperes per square centimeter of reaction surface at temperatures of $580^\circ - 750^\circ$ Abs. He found no current with the gases separately. He postulates nevertheless that the adsorbed gases are ionized by the "combined image and contact forces." A current of 1×10^{-16} amperes per square centimeter is an extremely minute one.

Becker⁵ has demonstrated the existence of both caesium atoms and ions upon the surface of a tungsten filament in the presence of vapor of that metal, and is able to estimate the proportion of each. He found that the wire attained a maximum in electron emission when covered with a monomolecular layer of caesium atoms. Below a certain critical temperature, a second adsorption layer started to build up.

Kunsman⁶ finds that the active Fe-Al₂O₃-Alkaline oxide catalysts (for ammonia) are excellent emitters of positive (alkali) ions. These catalysts

¹ Chem. and Ind., 46, 218 (1927).

² *Loc. cit.*

³ Proc. Roy. Soc., 116A, 379 (1927).

⁴ *Loc. cit.*

⁵ Phys. Rev., (2) 28, 341 (1926).

⁶ J. Franklin Inst., 203, 635 (1927).

give large and comparatively steady emissions. When Al_2O_3 is absent the emission is larger but less steady. He says, "It would seem quite reasonable, therefore, that one should look for a partial explanation, at least, of the increased catalytic activity of an $\text{Fe} - \text{Al}_2\text{O}_3$ - Alkaline oxide mixture to the presence of the alkali on the surface, either in terms of an interface phenomenon, a reduction of the electron work function of the surface, the emission of positive ions with a potential or neutral vapor without a potential." However, the presence of alkali decreases the activity of iron alone. He suggests that the alkali diffusing to the surface might act by keeping the surface in a state of constant eruption. If so, this effect would be present for iron alone. The effect of the alkali is very specific.

It is altogether possible that the presence of an ion would affect the reactivity of some molecules either by atomic distortion (already discussed), or by separating the atoms in case they differ in electrical polarity. The widespread catalytic effect of hydrogen ions may well be due to this cause.

Many of the foregoing experiments were conducted at elevated temperatures, where the thermal emission of electrons and ions is well enough established. These phenomena disappear at room temperature, except when enormous fields are applied to the surface. The experiments, therefore, cannot be used to demonstrate the existence of ions on the surface at room temperature. Furthermore, it is quite possible, in some of the experiments, that the substances do not exist upon the surfaces as ions, but that the ions are created by the very collision which ejects them from the surface. The writer's feeling is that to assume that substances are always adsorbed as ions, or that the preliminary formation of ions, is a prerequisite in catalytic processes is, to say the least, a very extreme view. At room temperature one might expect a molecule to remain unionized upon being adsorbed, at least in many cases, yet catalytic effects at room temperature are numerous.

Differential Heats of Adsorption

Some very interesting results have been obtained during the year by measuring the heat of adsorption for successive small portions of added gas.

Beebe¹ found that these "differential" heats of adsorption for carbon monoxide on copper were distinctly higher for the initial portions than for later portions. After accidental poisoning, resulting in decreased adsorptive capacity, the integral heat of adsorption was greater than on the unpoisoned catalyst. Beebe concluded that the most active points on the catalyst are not the most unsaturated ones.

Magnus and Kalberer² found that the heat of adsorption of carbon dioxide on wood charcoal was about 7450 calories at pressures greater than 5 mms., but rose to 12,460 calories at 0.076 mms. pressure. They interpreted this as being due to points of high adsorption potential. With carbon dioxide on silica, the heat of adsorption decreased linearly with increase in equilibrium pressure, which they attributed to the Joule-Thomson effect.

¹ J. Phys. Chem., 30, 1538 (1926).

² Z. anorg. allgem. Chem., 164, 345 (1927).

Garner¹ has found a maximum in the differential heat of adsorption curve for oxygen on charcoal.

Kistianowsky,² Taylor and Kistiakowsky,³ and Kistiakowsky, Flosdorf and Taylor,⁴ have found that the differential heat of adsorption of hydrogen on active copper and nickel catalysts is small for the first portions of gas adsorbed. It rises sharply to a maximum and then settles to a steady intermediate value as more gas is added. Heat treatment shifted the maximum toward smaller amounts of added gas, and made it less pronounced, and finally eliminated the maximum altogether.

When the catalyst was treated with oxygen, the initial value of the heat of adsorption was high, and there was no maximum. They interpret the results "as indicating in the active preparations a greater fraction of the surface capable of activating the adsorbed species, the activating process being endothermic, and possibly a dissociation into atoms. The heat treatment destroys these active areas on the surface preferentially."

This seems probable enough. However, they go on to say, "A difficulty of theoretical importance in connection with these results on the heat of adsorption on active catalysts may now be stated in the hope that some suggestions may be forthcoming as to its solution. It has been pointed out to us by Professor Herzfeld of Johns Hopkins University that, with the active preparations, the process first occurring is one in which the decrease in internal energy is very much less than that occurring subsequently at the maximum point and beyond. There is no evidence that the entropy changes involved would cause the free energy decrease at low adsorptions to be greater than those obtained at the maximum. The problem therefore arises as to why the process with a smaller free energy decrease should occur preferentially to that in which the large free energy decrease can take place."

The writer does not see the thermodynamic difficulty, and feels that multiple adsorption might account, at least in outline, for the results. There is a certain kinetic complexity involved in desorbing the multiply adsorbed molecule, which must be taken into account as well as the energy factor. This is not an unknown factor in thermodynamics for, according to the kinetic nature of the process, the terms involving the sum of the chemical constants can outweigh the term involving the heat of reaction in calculations of equilibrium.

Let us consider the molecules attached to the surface by two atoms. Judging from the distribution of the velocities of thermally emitted electrons, one can conclude that there is a Maxwellian distribution of energy amongst the surface atoms. There are two adsorption bonds to be broken before the adsorbed molecule can leave the surface. This can be done in two ways.

First, one atom can receive a thrust hard enough to endow it with sufficient energy to break both bonds. However, if E is the energy necessary to break

¹ Garner and McKie: *J. Chem. Soc.*, 130, 2451 (1927).

² *Proc. Nat. Acad. Sci.*, 13, 1 (1927).

³ *Z. physik. Chem.*, 125, 341 (1927).

⁴ *J. Am. Chem. Soc.*, 49, 2200 (1927).

each bond, the energy with which one atom must be endowed in order to break both bonds may be considerably greater than $2E$, for energy will be used up in stretching the adsorbed molecule.

The doubly adsorbed molecule can also leave the surface if each adsorbed atom receives a thrust endowing it with energy at least equal to E . However, in this case, unless both atoms receive this energy within a very short time, the first atom will be adsorbed again. It is a little difficult to calculate the exact magnitude of this effect. However, if the time interval within which both atoms must receive E is short enough, it is clear that the molecule will be desorbed less often than a singly adsorbed molecule whose energy of desorption is $2E$.

Amount of Adsorption and Catalytic Activity

Sabatschka and Moses¹ verify the point set forth at the beginning of this report that there is no quantitative correspondence between amount of total adsorption and catalytic activity.

Experiments of Griffin² also support this point.

However, Taylor and Kistiakowsky³ find that two active methanol catalysts show quite extraordinary adsorptive properties for hydrogen and carbon monoxide.

Intermediate Compounds

Sabatier,⁴ whose personal experience in catalysis is very great, appears to think that the formation of intermediate compounds is a satisfactory explanation of catalysis. However, his point of view does not remain unchallenged⁵ and one cannot restrain a desire to know what compounds are formed in specific instances (particularly when it seems unlikely that any orthodox compounds should be formed), and what there is about them which makes them so reactive. Perhaps a pursuit of such questions will lead to the fusion of the adsorption and intermediate compound points of view. There are cases where the hypothetical intermediate compounds cannot exist except on the surfaces. In these cases, perhaps, the postulate is unfruitful.

Zhukow⁶ has obtained some interesting results along this line. He heated a number of metals in nitrogen. Magnesium began to absorb nitrogen at 700° , Mg_3N_2 being formed; calcium reacted at the same temperature to form Ca_3N_2 ; lithium formed Li_3N . These three compounds show no measurable dissociation pressure below 1250° . With manganese and chromium, isotherms were obtained representing equilibria with solid phases of continuously varying composition (910° – 1200°). Aluminum began to form AlN at between 850° and 875° . Impure titanium behaves like manganese and chromium.

¹ Ber., 60B, 786 (1927).

² J. Am. Chem. Soc., 49, 2136 (1927).

³ J. Am. Chem. Soc., 49, 2468 (1927).

⁴ Ind. Eng. Chem., 18, 1005 (1926).

⁵ Boeseken: *Loc. cit.*

⁶ Ann. Inst. anal. physik. Chem., 3, 14 (1926).

Molybdenum absorbed only 20 cc. of nitrogen per five grams of metal, and uranium 27 cc. of nitrogen per four grams of metal at 1000°. No reaction below 1200° was observed with tungsten, zinc, copper, and iron. The electrical conduction of azotized chromium, manganese, and titanium was of the same order as that of the pure metals; that of AlN, Ca₃N₂, and Mg₃N₂ was less than 5×10^{-7} . There seems to be a distinct difference between the nitrides and the azotized metals.

Sabatier and Fernandez¹ have found that various difficultly reducible oxides are able to effect the hydrogenation and dehydration of organic compounds. Intermediate compounds seem rather a useless conception here.

According to Balareff,² alcohols merely add to phosphorus pentoxide below 130° forming normal phosphates and acid phosphates. No catalytic decomposition takes place. At 130°-150°, the addition still takes place, but the acid phosphate thus formed decomposes into ethylene and a volatile ester of phosphoric acid. At from 160°-260°, only part of the alcohol is combined with phosphorus pentoxide and catalysis takes place partly by formation of intermediate compounds and partly by adsorption and resulting thermal decomposition. At 390°, the alcohol is only adsorbed by the phosphorus pentoxide and the catalysis is accomplished not through the formation of intermediate compounds but by thermal dissociation of the adsorbed molecule. At this temperature no volatile ester of phosphoric acid is found in the reaction products. He considers that no sharp dividing line can be drawn between the two mechanisms.

Active Centers and the Structure of Surfaces

At the beginning of this report, it was set forth as an established fact that all catalytic surfaces are not uniformly active. Taylor,³ in the Fourth Report of the Committee on Contact Catalysis, developed the view that the most active centers are peaks of "extra lattice" atoms of high degree of unsaturation and that the edges and surfaces of crystals are less active according to their degree of unsaturation. This is a theory of catalytic surfaces, not of catalytic action, and Taylor did not claim otherwise for it. It does not qualify as a theory of catalysis because catalytic action at the peaks would be no more lucid than on a catalyst of uniform activity.

In the writer's opinion, the work on active centers (much of which is due to Taylor and his collaborators) by no means forces the conclusion that active centers are always necessary, nor even that when they exist they are peaks of "extra lattice" atoms, etc.⁴ The interfaces between minute crystals in a catalyst which without assumption must exist, would serve just as well as active centers. In other cases, the results apparently indicating active centers can be explained on plane surfaces.⁵ In still other cases,⁶ there is evidence

¹ Compt. rend., 185, 241 (1927).

² Z. anorg. allgem. Chem., 158, 105 (1926).

³ J. Phys. Chem., 30, 145 (1926).

⁴ J. Phys. Chem., 30, 1134 (1926).

⁵ This view is also held by Constable: Proc. Cambridge Phil. Soc., 23, 832 (1927).

⁶ Miss Wright: Proc. Cambridge Phil. Soc., 23, 187 (1927).

that the active centers consist of pairs of different atoms (predictable on the basis of multiple adsorption nevertheless, it has not been shown that Taylor's "extra lattice peaks," etc., never exist.

Constable¹ has decomposed copper salts of monobasic organic acids and investigated the catalytic action of the newly formed copper, measuring the rate of reaction by the rate of evolution of hydrogen. He concluded that the catalytic activity was independent of the nature of the compound from which the copper was derived.² He considers these results to agree with the hypothesis that the centers of activity of the surface are "frozen groups of atoms with strong specific external fields." This idea of an active center is not up to the standard of Constable's experimental work. If Constable objects to pursuing the question a little further and saying that on the grounds of the short range of surface forces, etc., multiple adsorption is a likely interpretation of the specificity, etc., of some active centers, he has not stated what his objections are. On the basis of the multiple adsorption mechanism, one would have some idea of how to set about creating *more* active centers.

In an investigation of the nature of the sintering of copper catalysts, Constable³ concluded that the coarse structures collapse even more easily than the fine ones, which he says shows that the energy present in the centers of activity is not very greatly in excess of that possessed by the regular arrangement of the surface atoms.

Miss Wright⁴ considers her data on the auto-oxidation of certain charcoals to show that the oxidation proceeds along chains of carbon atoms. The reaction is zero order, and only 0.38% is auto-oxidizable according to her measurements.

Rideal and Wright,⁵ in an investigation of the oxidation of oxalic acid by charcoal, consider that blood charcoal contains two types of active centers, which they think are Fe - C, and C - C complexes, and that sugar charcoal⁶ contains three types of active centers, attributed to Fe - C, C - C, and Fe - C - N complexes. They estimate the Fe - C complex to be 57 times as active as the C - C complex (on blood charcoal). The more active area on this charcoal was estimated, by the method of selective poisoning with KCN; to occupy 1.2% of the total surface area (estimated by Paneth's method, based upon the assumption that a surface is completely covered, one molecule deep, with methylene blue, when in the presence of that dye).

There are many points to be watched in the method of selective poisoning, e.g., steric effects not dependent upon the active centers; the quantity of poison must not be sufficient to cover the catalyst one molecule deep; one must be sure that the poison itself does not have some catalytic activity.

¹ Proc. Cambridge Phil. Soc., 23, 432 (1926).

² Compare the work of Adkins: Second Report of the Committee on Contact Catalysis.

³ J. Chem. Soc., 130, 1578 (1927).

⁴ *Loc. cit.*

⁵ J. Chem. Soc., 129, 3182 (1926).

⁶ J. Chem. Soc., 127, 1347 (1925); 129, 1813 (1926).

Rideal and Hoover¹ conclude that different patches upon thoria are active in the dehydrogenation and dehydration of ethyl alcohol.

According to Constable² reduced copper has an activity 8,000 times greater than that of electrolytic copper.

Bredig and Allolio³ conclude from X-ray studies that, except for particle size, there is no difference between the finely-divided, highly-active platinum, palladium, and nickel catalysts and inactive catalysts of these metals.

Madenwald, Henke, and Brown⁴ find that different preparations of lead, after use, assume the same activity for the hydrogenation of nitrobenzene. This may be purification of the surface, chemical change, or structural change.

According to Adam,⁵ it is unnecessary to suppose that liquefaction occurs at a surface upon polishing.⁶

Von Weimarn and Hagiwara⁷ claim that all rigid substances are crystalline. If amorphous patches in metallic catalysts are in all cases impossible it would be well worth knowing.⁸

Promoter Action

This is the name given to the phenomenon, sometimes observed, that the activity of a mixture of catalysts exceeds the additive effects of both. Promoter action, while of the greatest importance to catalysis in general, may be conveniently discussed in connection with the problem of the nature of active centers.

Constable⁹ has found that in the dehydration of alcohol over thoria, water acts as a promoter in small concentrations but becomes a poison at higher concentrations. This would be simply explained if the reaction occurred at the border between the water film and the underlying catalyst, a possibility which multiple adsorption suggests. Water would then become a poison as the film becomes complete in case the water itself has but small catalytic power for this reaction. Constable may not accept this explanation.

Kunsmann¹⁰ in an investigation of the thermal decomposition of ammonia on promoted iron catalysts found the heats of activation (using the time of half-life as a measure of the reaction rate) to be between 38,000 and 42,000 calories for all the catalysts examined, but that the catalytic activity varied as much as eighteen-fold. He concludes that the primary action of promoters is to increase the number of atoms upon which decomposition takes place and that heat treatment decreased this number; and that the quality of the centers upon which reaction takes place is not altered sufficiently to cause

¹ J. Am. Chem. Soc., 49, 104 (1927).

² Nature, 119, 349 (1927).

³ Z. physik. Chem., 126, 41 (1927).

⁴ J. Phys. Chem., 31, 862 (1927).

⁵ Nature, 119, 162 (1927).

⁶ Beilby: "Aggregation and Flow of Solids," (1921).

⁷ Kolloidchem. Beihefte, 23, 400 (1927).

⁸ See, however, Langmuir: J. Am. Chem. Soc., 2252 (1916).

⁹ Proc. Cambridge Phil. Soc., 23, 593 (1927).

¹⁰ Science, 65, 528 (1927).

an appreciable change in the heat of activation. He considers that the heat of activation may be a function only of the reacting gas and not of the catalyst.

The variation in the heat of activation which he records is sufficient to account for an eleven-fold change in rate, and it depends entirely upon the circumstances of the action (unpublished) whether the measured heat of activation can be taken as a measure of the true heat of activation or not. His last conclusion would seem most unlikely if the different catalysts lower the heat of activation of ammonia, and there is extremely good evidence¹ that they do. In promoter action as ordinarily defined, the quality of the active centers is changed, for the striking feature about promoter action is that the reaction velocity with the mixture is not that which would be expected by adding the velocities for the separate ingredients, nor by producing one new active center, of a kind effective on one of the separate ingredients, for each new particle of the new ingredient.

The thermal decomposition of ammonia upon platinum, at 100 mms. pressure, is retarded by hydrogen, but not by nitrogen. That on tungsten, is not retarded by hydrogen.² The decomposition upon molybdenum³ is retarded by nitrogen and not by hydrogen. It would be a good guess, therefore, that tungsten adsorbs the nitrogen atom of ammonia more strongly than the hydrogen atoms and vice-versa on platinum (there is considerable other evidence in support of this). On the basis of multiple adsorption, therefore, the decomposition of ammonia upon a mottled surface of tungsten and platinum should be more rapid than upon either alone. The writer⁴ has recently evaporated platinum from a spiral on to a tungsten filament in high vacuum, and found that the rate of decomposition on the mixed surface was unmistakably greater than on the underlying tungsten; and when tungsten was evaporated on to platinum, the activity of the mixed surface reached a value unmistakably greater than upon the underlying platinum. It is doubtful that the surface after the evaporation could accommodate many more molecules of ammonia than before. Although the experiments have not been completed, this seems a clear case of promoter action which was predicted theoretically. The magnitude of the promoter action was not as great as is often found (the rates on the mixed surfaces were about twice as great as upon the unalloyed surfaces).

Almquist,⁵ also, thinks that the main function of promoters is to increase the number of catalytically active atoms. Again, he must define promoter action differently from the writer.

Quartaroli⁶ has found that $Mg(OH)_2$, $Cd(OH)_2$ and $Ni(OH)_2$ greatly diminish the rate of decomposition of alkaline hydrogen peroxide and greatly diminish the power of $Pb(OH)_2$ to accelerate the decomposition of the sub-

¹ Discussed under "Lowering of the Heat Activation."

² Hinshelwood and Burk: *J. Chem. Soc.*, 127, 1105 (1925).

³ Burk: *Proc. Nat. Acad. Sci.*, 13, 67 (1927).

⁴ Experiments soon to be published.

⁵ *J. Am. Chem. Soc.*, 48, 2820 (1926).

⁶ *Gazz.*, 57, 234 (1927).

stance. But these same compounds greatly increase the accelerating action of Ag_2O on the decomposition of hydrogen peroxide. Quartaroli's explanation is that the added substances protect or destroy the real catalyst (not named).

Yant and Hawk¹ have investigated the catalytic oxidation of methane by metals and oxides and mixtures of these. Promoter action was not the rule here, although mixtures of Co_2O_3 and nickel were almost as efficient as Co_2O_3 alone, nickel alone being quite inefficient.

Taylor and Kistiakowsky² say, "The mode of action of promoters can be traced to the following causes, (1) protection of the catalyst from sintering, and in this way the adsorbing surface, especially the number of unsaturated atoms; (2) the place of contact between different chemical substances may be the seat of special actions upon the adsorbed molecules and thereby give rise to selective effects; (3) the possibility is not excluded that the added substance has chemical action, e.g., in breaking up the intermediate compound formed with the catalyst." In point (1) these authors are considering phenomena different from true promoter action, as defined above for one particular phenomenon, e.g., the effect of "supports" may be in part that given in (1). It seems to the writer that the most likely interpretation of point (2) is multiple adsorption.³ Surely the promoter effect would not be attributed to the force at a mathematical dividing line between two atoms. The individual forces of the two atoms will be the more intense the nearer one approaches the respective atoms. The effective specific force would then become a pair of forces with definite strength and spacing dependent upon the nature of the individual atoms. Promoter action is a most natural consequence of multiple adsorption.⁴ It is a little difficult to say what the profitable attitude⁵ toward point (3) should be. When there is more than one molecule reacting, the promoter may act simply by placing the second molecule in a suitable juxtaposition more frequently.⁶

Supported Catalysts

Tropsch⁷ has found that at 355° the dissociation of formic acid (water-free) to carbon dioxide and hydrogen occurs most readily over tinned iron.

There is a possibility regarding supported catalysts which does not seem to have been recognized. The possibility is that in addition to the prevention of sintering, in the case of thin films, as in the foregoing instance, the support can enforce its spacing upon the catalyst film, which may be more suitable than the normal spacing of the catalyst. Morris and Reyerson⁸ have found

¹ J. Am. Chem. Soc., 49, 1454 (1927).

² Z. physik. Chem., 341, 125 (1927).

³ See the experiments upon the thermal decomposition of ammonia described above.

⁴ Burk: J. Phys. Chem., 30, 1134 (1926).

⁵ See the discussion of intermediate compounds in this report.

⁶ Rideal and Taylor: "Catalysis in Theory and Practice," p. 31 (1919); Langmuir (Trans. Faraday Soc., 17, 607 (1922)) discusses this type of spacing effect. See also Hinshelwood: "Kinetics of Chemical Change in Gaseous Systems," p. 195 (1926).

⁷ Abhandl. Kenntnis Kohle, 7, 1 (1925); Chem. Abs., 21, 3530 (1927).

⁸ J. Phys. Chem., 31, 1220 (1927); 32, 113 (1928).

that thin films of metals upon silica gel have marked catalytic activity; whereas, the experiments of Gauger¹ will be recalled who found thin films of nickel or platinum on Pyrex to be inactive (there is no apparent reason for "extra lattice" atoms to be precluded on the Pyrex-metal films.)

Films on Catalysts

The rather disheartening point arises that the real catalysts may not be what we think they are. The writer has observed that if a tungsten wire, which is in a perfectly steady state of activity for decomposing ammonia, be heated, at the same temperature used for decomposition, in a high vacuum, its activity falls off markedly, but is regained upon decomposing more ammonia. The steadiness which the wire attains—which is easily reproduced—would make an actual change in structure with decomposition unlikely (though not impossible) in this case. The probable explanation is that the tungsten becomes covered with a film of nitrogen, possibly atomic. This conclusion is supported by the work of Kenty and Turner² who find that active nitrogen produces a film on tungsten, when this metal is maintained at dull red heat. The writer has also found evidence for the existence of a similar film upon molybdenum³ when used for the thermal decomposition of ammonia.

Bone and Forshaw⁴ find that the catalytic action of fireclay upon the combustion of carbon monoxide and hydrogen is stimulated by previous exposure to the combustible gases.

Spitalsky⁵ found that electrochemical pretreatment of platinum with oxygen decreased its activity in decomposing hydrogen peroxide, while cathodic polarization increased it. Thus a film of hydrogen on platinum has a beneficial effect when used for this reaction, and a detrimental effect when used for the decomposition of ammonia.

There is much evidence to show that many catalysts behave quite differently when the films of moisture are removed from them.⁶

Langmuir has shown how tenaciously films of oxygen are attached to tungsten.⁷

Clark and Topley⁸ encounter the film question in experiments on the catalytic decomposition of formic acid.

The point has been subjected to special investigation for the case of water synthesis over nickel by Hughes and Bevan.⁹

¹ J. Amer. Chem. Soc., 47, 2278 (1925).

² Nature, 120, 332 (1927).

³ Proc. Nat. Acad. Sci., 13, 67 (1927). Portions of this paper have been called into question, and the research has not been fully repeated.

⁴ Proc. Roy. Soc., 114A, 169 (1927).

⁵ Ber., 59, 2900 (1926).

⁶ Bone: Proc. Roy. Soc., 112A, 477 (1926).

⁷ Trans. Faraday Soc., 17, 618 (1922).

⁸ J. Phys. Chem., 32, 121 (1928).

⁹ Proc. Roy. Soc., 117A, 101 (1927).

It is therefore well to consider whether a given catalyst is ordinarily bare (except for loosely adsorbed substances), or whether the reaction is probably taking place on a stable film, which may vary in nature according to the reaction catalyzed.

Poisons

Constable¹ has investigated the effect of inert diluents on the rate of decomposition of alcohol over copper; he found their behavior to fit his previously deduced formula.² If the heat of adsorption of the reactant is greater than that of the diluent, the temperature coefficient of the reaction is less than the true one, and vice versa. He says, "this is a hitherto unsuspected cause of error in temperature coefficient measurement." The point is well taken, but is not new.³

Selective poisoning has been discussed under "active centers." There is nothing very mysterious about the action of poisons.

Dust Particles

According to Rice⁴ many reactions would take on a different aspect if extreme precautions were taken to remove dust particles which act as catalysts. Rice and Kilpatrick⁵ find the decomposition of hydrogen peroxide to be such a reaction. Rice and Getz⁶ find that the thermal decomposition of nitrogen pentoxide is unaffected by carefully removing the dust particles.

The reactions which have been found to be homogeneous and kinetically accountable would not be expected to depend upon the presence of dust particles. It would not seem that dust particles offer a very great menace to the sound investigation of reaction velocity; surely dust particles cannot be universally effective as catalysts, and their effectiveness would not often be expected to compare in magnitude with that of the walls, which are probably similarly constituted, and of larger area, and with that of added specific catalysts.

Moisture

The catalytic effect of water vapor stands in a similar, though probably more important position.

Garner and Johnson⁷ find that the presence of moisture greatly depresses the emission of infra-red radiation from exploding carbon monoxide-oxygen mixtures. Their interpretation is that the water increases the rate at which thermal equilibrium is reached, energy being conserved which otherwise would be radiated away. They call this "energo-thermic" catalysis. If the energy is used merely to raise the temperature of the system, it is questionable whether it should be considered a special type of catalysis, any more

¹ Proc. Cambridge Phil. Soc., 23, 593 (1927).

² Proc. Cambridge Phil. Soc., 23, 172 (1926).

³ Hinshelwood: "Kinetics of Chemical Change in Gaseous Systems," 178 (1926).

⁴ See Fifth Report of the Committee on Contact Catalysis.

⁵ J. Phys. Chem., 31, 1507 (1927).

⁶ J. Phys. Chem., 31, 1572 (1927).

⁷ Phil. Mag., 3, 97 (1927).

than highly reflecting walls should be. The authors did not state whether or not they considered water molecules to be necessary in the sphere of reaction.

Armstrong¹ denies that water in this reaction reacts directly with the carbon monoxide. His objection is discussed later.

New experiments of Smits² indicate that the density of dried ammonium chloride is greater, and the vapor pressure smaller than for the moist substance below 300°C. He considers that his experiments show that intensive drying causes a shift in an inner equilibrium.

Now the amount of moisture which will cause ammonium chloride to behave normally is less than one part in a million, as the writer knows from personal experience with this problem. This amount of moisture cannot cause decided shift in an equilibrium by reacting with one of the species. If the change in the equilibrium is caused in some other way, it would seem that a negligible free energy of reaction would have to be assumed, or that an enormous amount of energy would be involved in removing the last traces of water. The explanation in general does not strike one as plausible. In an earlier paper, in discussing the possibility of the displacement of an equilibrium Smits³ says, "It is tacitly assumed that a trace of moisture can displace the inner equilibrium to a very considerable extent, the thermodynamic significance of which is, that a very large amount of work is necessary to withdraw the last trace of water from the substance, and this is not improbable." He does not say why it is not improbable, and it certainly seems improbable on the face of it.

Smits⁴ has also found that intensive drying increases the vapor pressure of nitrogen tetroxide by as much as 3.5 cms., the change being accompanied by a deepening of the brown color. He found intensive drying to decrease the vapor pressure of hexane, benzene, carbon tetrachloride, and carbon disulphide. Again he suggests shifts in the inner equilibrium.

Smith⁵ also found that intensive drying increases the vapor pressure of nitrogen tetroxide and agrees with Smits as to interpretation.

Balareff⁶ found that after standing in contact with phosphorus pentoxide for three and one-half years, methyl alcohol, ethyl alcohol, benzene, hexane, and ether had added phosphorus pentoxide forming phosphates, which remained as a residue after evaporating the liquid. He thinks these addition compounds, or phosphates, may account for the results on the change of vapor pressure of liquids with intensive drying. However, Baker⁷ says his experiments do not admit this possibility.

¹ Nature, 120, 659 (1927).

² Rec. Trav. chim., 46, 445 (1927).

³ J. Chem. Soc., 125, 1069 (1924).

⁴ J. Chem. Soc., 129, 2655 (1926).

⁵ J. Chem. Soc., 130, 867 (1927).

⁶ J. prakt. Chem., 116, 57 (1927).

⁷ J. Chem. Soc., 130, 2902 (1927).

Briner¹ has performed experiments which make him doubt that water plays an essential part in the oxidation of nitric oxide, a result previously reported with not too great certainty by Baker². This is not the first time Baker's results have been called into question,³ and he has made good his claims on the other occasions.⁴ Nevertheless, the oxidation of nitric oxide is a homogeneous reaction satisfactorily accounted for kinetically,⁵ and there is, therefore, no reason for expecting it to depend upon the presence of water-vapor. Briner points out that the velocity of this homogeneous reaction is greatest at liquid air temperatures, where the concentration of water-vapor is extremely small.

According to experiments of Cohen and Heymer,⁶ the combination of hydrogen and chlorine is not a wall effect, and the inhibition observed upon drying, therefore, cannot depend upon removing the water from the walls.

Negative Catalysts or Inhibitors

Bäckström⁷ has carried out some interesting experiments on negative catalysis in the oxidation of aldehydes and of sodium sulphite. He found negative catalysis both for the light and dark reactions, and found quantum efficiencies for the light reactions of the order of 10,000-50,000 molecules per quantum. His results led him to come out for Christiansen's theory of negative catalysis.

Christiansen's theory⁸ is an extension of his "hot molecule" mechanism,⁹ which he used to account for reactions with otherwise necessary high rates of activation. The idea has been shown theoretically by Tolman¹⁰ to be of doubtful value for some types of reactions, and has been shown experimentally by Hinshelwood and Hughes¹¹ to be most improbable in the favorable case of the thermal decomposition of chlorine monoxide (which easily becomes explosive).

Christiansen believes that because the molecules of reaction products, when first formed, possess high energy content, they can activate new molecules of reactant at the first encounter, the process being repeated, thus giving rise to long reaction chains. He then proposes that negative catalysts act by breaking up these chains, either by taking up the energy from the "hot" molecules of reaction products, or by reacting with them in some way or other.

¹ *J. Chim. phys.*, 23, 848 (1926).

² *J. Chem. Soc.*, 65, 613 (1894).

³ Gutmann: *Ann.*, 299, 267 (1898).

⁴ Baker: *J. Chem. Soc.*, 73, 422 (1898).

⁵ Bodenstein: *Z. physik. Chem.*, 100, 68 (1922).

⁶ *Ber.*, 59B, 1794 (1926).

⁷ *J. Am. Chem. Soc.*, 49, 1460 (1927).

⁸ *J. Phys. Chem.*, 28, 145 (1924).

⁹ Christiansen and Kramers: *Z. physik. Chem.*, 104, 451 (1923).

¹⁰ *J. Am. Chem. Soc.*, 47, 1524 (1925).

¹¹ *J. Chem. Soc.*, 125, 1841 (1924). See also Hinshelwood: *Chem. Rev.*, 3, 227 (1926).

The writer feels that there are certain objections to such a mechanism for negative catalysis, in addition to those referred to above, and others¹ for the general scheme of "hot" molecule chains in slow thermal reactions, which should be disposed of before accepting the chain mechanism in any specific case. First, the amounts of negative catalyst necessary are often minute, which in the ordinary case would seem to rule out reaction with the "hot" molecules, because the supply of negative catalyst would soon be used up.² Secondly, there are present, after the reaction has proceeded a small distance, molecules of products in enormously greater numbers than those of the negative catalyst. These would also rob the newly formed molecules of products of their energy, and while it may be argued that they would then be as effective as the original "hot" molecules of products in activating new reactant molecules, nevertheless, if the energy passes from product molecule to product molecule in this way before being transferred to a reactant molecule, the chance of breaking up the chain through distribution of the energy would be very great. The transfer in this way from product molecule to product molecule cannot be ruled out on the grounds of specificity in the transfer of energy on collision, since they are molecules of the same kind. Thirdly, if the molecules of negative catalyst really do rob the "hot" product molecules of their energy, they would, as far as the writer can see, be on precisely the same basis as molecules of products, unless additional assumptions are made, and could communicate the "stolen" energy to reactants as well as the "hot" molecules whose energy they have just taken up.³ It is not true in general that the molecules of inhibitor are more complicated than the molecules of product, which might otherwise cast doubt upon this possibility. In other words, if the "cold" products do not themselves act as negative catalysts, why should the negative catalysts act as such?

The old and simple idea that a negative catalyst acts by destroying the activity of a positive catalyst is difficult to dispose⁴ of, and its incompetence must be shown in each individual case, when negative catalysis is restricted to the case of a given reaction actually being slowed up (not replaced by faster side reactions, etc.).

F. Perrin⁵ considers the action of antioxygens to consist in the selective deactivation of the active molecules.

Mujamoto⁶ has found that the velocities of oxidation of mixtures of stannous chloride and sodium sulphite in sodium hydroxide solution are

¹ E.g., with a reaction of the type $A = A' = R'$, $+ A = A' + R$, A' and R' are probably indistinguishable for the purposes of reaction velocity so that the whole theory loses point in this case.

² (Note added to the proof.) Prof. H. S. Taylor informs me that since the completion of this manuscript, a great many results have been obtained in his laboratory which can best be interpreted in terms of the chain mechanism. The inhibitor, or negative catalyst, in some of these experiments was itself destroyed by oxidation, but at an extremely slow rate. (One molecule for some fifty thousand molecules of sulphite normally oxidized). The very slow endothermic destruction of the inhibitor would also account for a point raised at the end of this paragraph.

³ See, however, footnote 2.

⁴ See the section on moisture in this Report.

⁵ Compt. rend., 184, 1121 (1927).

⁶ Bull. Chem. Soc., Japan, 2, 191 (1927).

less than those of either alone, except when the concentration of stannous chloride is low.

Cases of negative catalysis found by Tropisch and von Philippovich¹ and by Quartaroli² have been discussed under "promoter action."

Homogeneous Catalysis

Since contact catalysis is the subject of this report, homogeneous catalysis will not be elaborately considered. Nevertheless, an account of the status of contact catalysis would suffer if homogeneous catalysis were completely neglected.

Dawson³ and his co-workers have carried out an extensive series of investigations on catalysis in solution. Some of their conclusions are the following. The "proton" theory of chemical reactivity is inconsistent with the facts. Catalytic effects must be attributed to the hydrogen ion, the undissociated acid, the acid ion, and the hydroxyl ion. Catalytic activity is proportional to the volume concentration of molecular or ionic catalyst, and has no apparent connection with the thermodynamic activity.

Skrabal,⁴ also, takes into consideration the catalytic activity of water molecules, of hydrogen ions, and of hydroxyl ions. He finds that the catalytic effect of hydrogen ions is relatively constant (for the saponification of different esters) but that the catalytic effect of the hydroxyl ions varies over extremely wide limits. It is interesting in this connection, that an association related to multiple adsorption is possible for the hydroxyl ion but not for the hydrogen ion.

Brønsted and Guggenheim⁵ do not ascribe the catalytic activity of acids and bases to the hydrogen and hydroxyl ions, but to the acid and base molecules. The catalytic efficiencies of acids and bases were found to be proportional to their strengths (for the mutarotation of glucose).

Bergstein and Kilpatrick⁶ and Bergstein⁶ find that the catalytic minimum point (the point of minimum velocity), for the reaction between iodine and acetone, was not displaced by neutral salts, nor by temperatures within the limits 25°-45°. They find the reaction to be complex, and were unable to identify all the catalysts with certainty.

According to Baudisch and Davidson,⁷ the ferrate and ferrite ions have identical catalytic activity for the oxidation of certain organic compounds.

Kiss and Zombory⁸ think that the reaction, $S_2O_8^{2-} + 2I^- = 2SO_4 + I_2$, catalyzed by iron ions, takes place in accordance with the mechanism:

¹ *Loc. cit.*

² Dawson and Hoskins: *Proc. Leeds Phil. Let. Sci. Sect.*, 1, 108 (1926); Dawson and Dean: *J. Chem. Soc.*, 129, 2872 (1926); Dawson and Carter: 129, 2282 (1926); Dawson: 130, 458, 1290 (1927); *J. Phys. Chem.*, 31, 1400 (1927).

³ *Z. Elektrochemie*, 33, 322 (1927).

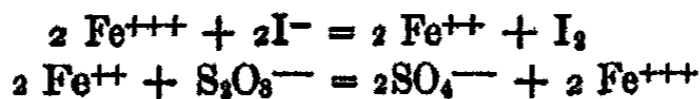
⁴ *J. Am. Chem. Soc.*, 49, 2554 (1927).

⁵ *J. Phys. Chem.*, 30, 1616 (1926).

⁶ *J. Phys. Chem.*, 31, 178 (1927).

⁷ *J. Biol. Chem.*, 71, 501 (1927).

⁸ *Rec. Trav. chim.*, 46, 225 (1927).



Åkerlöf¹ and others have attempted to correlate reaction velocities in solution with the activities of the catalysts. For the decomposition of diacetone alcohol, Åkerlöf finds that the reaction velocity is proportional to the activity of the catalyst when the latter is potassium hydroxide, or sodium hydroxide. When lithium hydroxide is the catalyst, however, the velocity is accurately proportional to the concentration and not to the activity. He was unable to obtain a definite relationship between activity and reaction velocity for the hydrolysis of ethyl acetate and of cyanamide. A great many straight lines are shown in the paper with only two points on them.

Thermodynamics is not concerned with the rates at which systems approach equilibrium. If activities are the numerical coefficients which one must substitute for concentrations for thermodynamical purposes, it would seem that they should be irrelevant to the subject of reaction velocity, and that the volume concentration, *a priori*, should be the important thing, for it is the volume concentration which comes into the expression for the number of collisions. If the non-ideal behavior of one species dissolved in another is due entirely to the real concentration not being what we think it is, and if the activity coefficient is a measure of this divergence and of nothing else, then one should use activities in expressions for reaction velocity—otherwise, not. If a single molecule can exhibit different activities in different thermodynamic environments, as presumably it can, then the activity coefficients cannot be an index to the true concentration of the dissolved species and to nothing else since this value (which is real in contradistinction to the temperature of a single molecule), is constant, or zero, in the various thermodynamic environments.²

Heat of Reaction and Catalytic Mechanisms

There is another point of confusion in the use of thermodynamics in reaction velocity work, namely, one finds statements that certain reactions are probable or impossible on the basis of the value of the corresponding heat of reaction. The question is, of the two reactions,

- (1) $\text{AR} = \text{AR}_1 + \text{R}_2$ and
 (2) $\text{AR} = \text{AR}_3 + \text{R}_4$,

can we predict from a knowledge of thermodynamic quantities which will take place in preference to the other? That (1) will take place in preference to (2) simply means that under the given conditions, the rate of (1) is large compared to that of (2). The very existence of endothermic reactions is proof enough that the value of the heat of reaction is not an index to reaction velocity. The very existence, for instance, of hydrogen-oxygen gas mixtures at room temperature is proof enough that the free energy of reaction is not the determining factor in reaction rate.

¹ J. Am. Chem. Soc., 49, 2956 (1927).

² Compare Dawson and Dean: *Loc. cit.*

It can easily be shown that in accordance with the theory of reaction velocity as given in this report, the heat of reaction is equal to the difference in the heats of activation of the direct and reverse reactions. Therefore, the only condition under which the heat of reaction has any significance for reaction velocity is when the heat of activation of the direct or reverse reaction is known. Thus, if it can be shown that the heat of activation in one direction is zero (as may be possible, e.g., in the combination of some atoms), then the heat of reaction can be substituted directly for the heat of activation in the velocity expression for the reverse reaction. The heat of reaction must, however, be at least as small as the largest heat of activation which can be allowed in the case of a given endothermic reaction proceeding at a given rate at a given temperature.

Therefore, without special knowledge, the value of the heat of reaction is no argument that a given mechanism is probable.

Nor can such an argument be used against any mechanism. Thus, Armstrong¹ says the mechanism $\text{CO} + \text{OH}_2 = \text{CO}_2 + \text{H}_2$, originally advanced by Dixon to explain the rôle of water in accelerating the combustion of carbon monoxide, "is precluded by the fact that the heat of combustion of hydrogen to liquid water is greater than that of carbonic oxide."

Kapanna² has found that in the conversion of NH_4CNS to $\text{SC}(\text{NH}_2)_2$, the direct and reverse reactions are of the first order, and are uncatalyzed by glass wool and platinum strips. He found the difference in heats of activation to be equal to the heat of reaction.

Simultaneous Reactions

These reactions are of great theoretical and practical interest. It is often found that, of two possible modes of decomposition of a molecule, some catalysts accelerate one almost exclusively, different ones accelerate the other almost exclusively, and still others accelerate both.³

Clark and Topley⁴ have decomposed formic acid on several new catalysts. The various researches with this substance have not enabled the investigators to correlate the velocity of its modes of decomposition on different catalysts with the respective heats of activation. Differences in adsorption relations can, however, account for the discrepancies.⁵

Senderens⁶ has found that the decomposition of formic acid in the wet way by sulphuric acid, potassium sulphate, and ortho-phosphoric acid is purely catalytic; that is, the action is not merely the taking up of the water formed. The sole products are carbon monoxide and water. In the dry way, Senderens says alumina gives carbon monoxide and water at 200°-250°, but thoria gives carbon dioxide and formaldehyde. Particular attention should

¹ Nature, 120, 659 (1927).

² Quar. J. Indian Chem. Soc., 4, 217 (1927).

³ See the reference in the introduction to this report.

⁴ J. Phys. Chem., 32, 121 (1928).

⁵ Hinshelwood: "Kinetics of Chemical Change in Gaseous Systems," 181 (1926).

⁶ Compt. rend., 184, 856 (1927).

be called to the fact that both of the latter catalysts are compounds of the same type, namely, difficultly reducible oxides.

According to Tropsch¹ the decomposition of anhydrous formic acid to carbon dioxide and hydrogen, at 355°, occurred most readily over iron, and tinned iron. At 255° with tinned iron, formic acid decomposed to carbon monoxide plus hydrogen and small quantities of methane. Glass wool, asbestos, and pumice, at 355°, formed both carbon monoxide and dioxide, as did calcium carbonate at 400°, and lithium carbonate at 255°-410°, and ThO₂ at 355°. Alumina at 305° and 435° formed almost exclusively carbon monoxide and water, whether the formic acid was dry, or contained water-vapor. In particular, the results with tinned iron should be noticed.

According to Müller and Hentschel,² the decomposition of formic acid by ultra-violet light in the presence of highly dispersed platinum falls off greatly when the latter becomes aggregated. In boiling aqueous solutions, the reaction yields carbon dioxide and hydrogen, and also water and carbon monoxide.

According to Tropsch and Roehlen,³ the catalytic decomposition of formaldehyde was very rapid at 300°-500° over sodium carbonate, calcium carbonate, barium carbonate, zinc oxide, alumina, thoria, chromium oxide, uranium oxide, alkalyzed iron, and lead, but not over quartz or antimony. Lead was the best catalyst. Considerable methyl alcohol was formed over thoria, alumina, uranium oxide, sodium carbonate and activated carbon. Formation of methane occurred especially with chromium oxide and with activated carbon, while the formation of unsaturated hydrocarbons occurred with alumina. A five percent yield of formic acid was obtained with uranium oxide. Zinc oxide gave few reaction products of high molecular weight; it decomposed dry formaldehyde smoothly to carbon monoxide and hydrogen, and moist formaldehyde smoothly to carbon dioxide and (hydrogen?). The latter is a very striking result.

Tinned iron, whose properties in the decomposition of formic acid were so remarkable, had but slight effect on the decomposition of methyl alcohol.⁴ The decomposition products with this catalyst, and with iron, tin, and aluminum at 520° contained considerable quantities of carbon dioxide, carbon monoxide, hydrogen, and methane.

According to Sabatier,⁵ thoria, alumina, and the blue oxide of tungsten, active in the catalytic decomposition of methanol, accelerate almost exclusively the reaction



while MnO gives dehydrogenation, like the metals. Other oxides produce both effects simultaneously. The action of zinc oxide upon ethyl alcohol is

¹ Abhandl. Kenntnis Kohle, 7, 1 (1925); Chem. Abs., 21, 3530 (1927).

² Ber., 59, 1854 (1926).

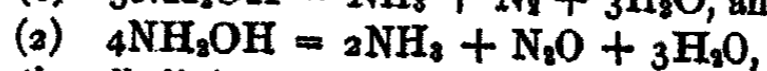
³ Abhandl. Kenntnis Kohle, 7, 15 (1925); Chem. Abs., 21, 3530 (1927).

⁴ Tropsch and Schellenberg: Abhandl. Kenntnis Kohle, 7, 13 (1925); chem. abs., 21, 3530 (1927).

⁵ Compt. rend., 185, 17 (1927).

principally dehydrogenation, while that of chromium oxide is principally dehydration. Both reactions are almost equal with zirconia and glucina.

According to Kurtenacker and Werner,¹ in the decomposition of hydroxylamine, the ratio of the two reactions



was controlled by the alkalinity. Platinum black favors (2), while platinum sponge, or platinum gauze does not affect the proportions of the end products.

Mutiple adsorption seems particularly apt in explaining the effect of catalysts in selectively catalyzing one of two or more possible reactions of a compound, since on this mechanism a particular bond can be separately stretched. It is not so obvious that the atomic distortion theory can account for the results, especially when very specific and different effects are produced by compounds ionically of the same kind.

The Thermal Decomposition of Ammonia

Certain reactions, for one reason or another, have received a particular amount of attention. One of these is the thermal decomposition of ammonia. Reasons have already been given that the lowering of the heat of activation is the only effect of tungsten in catalyzing this reaction, and that the real catalyst in this case is a film of nitrogen upon the tungsten. The results of Kunsman have been described under "promoter action," as have some unpublished results of the writer. The writer² has found that the thermal decomposition of ammonia upon molybdenum is somewhat retarded by nitrogen, but not by hydrogen. It developed in this investigation that the cases of a poison blocking certain active centers completely, and leaving others free, and of a poison covering the entire catalyst, but itself having some catalytic activity, lead to equations of the same form expressing the reaction velocity.

Schwab³ has decomposed ammonia upon heated strips of platinum and tungsten, and compared the behavior with that found by Hinshelwood and Burk.⁴ Schwab's work was at pressures of the order of 0.01 mm. while the latter was at pressures some 10,000 times as great. At low pressures, the decomposition on both platinum and tungsten was found to be monomolecular; at the higher pressure, the decomposition on tungsten is zero order. Nitrogen was found to retard both reactions at the low pressure; at the higher pressure it retards neither the reaction on platinum, nor that on tungsten. Hydrogen was found to retard both reactions at the low pressures, but at the higher pressure, retards only the reaction on platinum. The temperature coefficients did not agree in the two researches. This is probably to be explained by the different poisoning phenomena.

¹ Z. anorg. allgem. Chem., 160, 333 (1927).

² Proc. Nat. Acad. Sci., 13, 67 (1927).

³ Z. physik. Chem., 128, 161 (1927).

⁴ J. Chem. Soc., 127, 1105 (1925).

These results are not surprising when one takes into consideration the knowledge of catalysts, of variable surface films, etc. Thus the nitrogen film on tungsten may be completely formed at 100 mms. but not at 0.01 mms. The film at the low pressures may be of a different structure, and have different properties from that at the higher pressures. The gases may poison certain centers at the low pressures in proportion to their pressure. At the higher pressures, these centers may be blocked out almost from the start, and poisoning upon others may not yet have set in. Schwab considers similar explanations, but also considers multimolecular layers possible. He appears to consider the reaction to take place by collision from the gas phase. This could not be the mechanism, or the reaction on tungsten could not become zero order at the higher pressure, as it does.

The Decomposition of Hydrogen Peroxide

Kiss and Lederer¹ find that metals of invariable valence—calcium, cadmium, magnesium, strontium, and zinc—were without action upon the decomposition of hydrogen peroxide. However, the action of cobalt, manganese, and nickel, also, was so small that it was attributed to impurities (copper or iron). The action of copper and iron was very marked. They suggest a mechanism involving the rather strange assumption that molecular addition is the slow reaction. Their mechanism involves change in valence for both the copper and iron. The change in valence of the copper was thought to be shown by the color change of the solution.

According to Spitalsky and Funck,² the behavior of sodium molybdate as a catalyst for the decomposition of hydrogen peroxide depends upon whether it is in a stable state or not. This compound is thought to go over to the catalytically stable state by a preliminary reaction with hydrogen peroxide, and is rendered unstable again after a definite time, which is conditioned by the slow formation, and very slow decomposition, of an intermediate compound.

According to Piszarshevskii and Roiter,³ the decomposition of hydrogen peroxide in solution is a unimolecular process. They consider the nature of the mechanism to be the same whether platinum, or manganese dioxide is used as a catalyst.

Spitalsky and Koboseff⁴ think it necessary to assume more than one intermediate compound in order to explain all the known results for the catalytic decomposition of hydrogen peroxide by chromic acid.

Elder and Rideal⁵ decomposed pure hydrogen peroxide vapor on quartz, platinum, and mercury. On quartz at 85°, the reaction was found to be zero order, inhibited by oxygen. This reaction stopped 80% short of completion. On platinum wire, the apparent order of the decomposition was the first,

¹ Rec. Trav. chim., 46, 453 (1927).

² Z. physik. Chem., 126, 1 (1927).

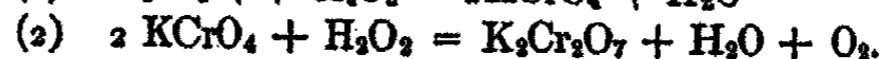
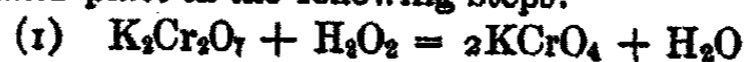
³ Sci. Mag. Chem. Cath. Katerinoslav, 93 (1926); Chem. Abs., 21, 2414 (1927).

⁴ Z. physik. Chem., 127, 129 (1927).

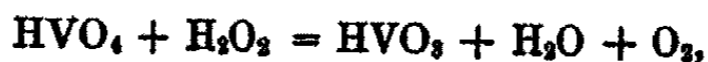
⁵ Trans. Faraday Soc., 23, 545 (1927).

which they consider to be determined probably by the rate of diffusion through an adsorbed or dissolved layer of oxygen. The reaction on a mercury surface was thought to consist of a preliminary direct oxidation to Hg_2O , followed by a coupled oxidation to HgO .

According to Robertson,¹ the catalytic decomposition of hydrogen peroxide by $\text{K}_2\text{Cr}_2\text{O}_7$ takes place in the following steps:



HVO_3 is thought to act as a negative catalyst because the rapid reaction (2) is superseded by



HVO_4 being produced by oxidation of HVO_3 by H_2O_2 ; it is not clear why a rapid reaction should be superseded by a slow one.

The catalysis of this reaction by $\text{K}_2\text{Cr}_2\text{O}_7$ is promoted by MnCl_2 .² Robertson considers the shape of the curves for the promoted reaction to show the presence of two superimposed first order reactions, one related to the concentration of intermediate compound due to the promoter. (The nature of this intermediate compound could not be determined by absorption spectral measurements). The other monomolecular reaction he considers related to the velocity constant of the promoted reaction.

For other results on hydrogen peroxide, see the discussions of "promoter action," and "dust particles."

Water Synthesis

Benton and Elgin³ have found that in the synthesis of water over gold, the rate of reaction varied as the square of the hydrogen pressure, as the first power of the oxygen pressure, and inversely as the water vapor pressure. Independent adsorption measurements showed hydrogen not to be adsorbed appreciably, while oxygen is strongly adsorbed. They say: "A mechanism based on the interaction of adsorbed oxygen with two hydrogens adsorbed on adjacent spaces on the catalyst surface will not account for the observed kinetics, since it may readily be shown that with the relative adsorptions found for the two gases, this assumption requires the velocity to be proportional to the square of the hydrogen pressure and to the inverse first power of the oxygen pressure." One must be very careful in drawing such conclusions from independent measurements of adsorption.⁴

In a previous work, these authors⁵ considered the same reaction over silver to involve collisions of gaseous hydrogen with adsorbed oxygen on the fraction of the surface not covered by water. They could have settled this point definitely had they used a selectively heated catalyst, and varied the bulb temperature. In case the reaction does not take place by collision from

¹ Proc. Nat. Acad. Sci., 13, 192 (1927).

² J. Am. Chem. Soc., 49, 1630 (1927).

³ J. Am. Chem. Soc., 49, 2426 (1927).

⁴ Compare Hinshelwood and Prichard: J. Chem. Soc., 127, 806 (1925).

⁵ J. Am. Chem. Soc., 48, 3027 (1927).

the gas phase, this variation in bulb temperature would, ordinarily, be without great effect upon the reaction velocity.

Remy¹ has investigated this reaction extensively, using metals of group eight as catalysts. He assumes, with Hoffmann,² that both hydrogen and oxygen, in the water synthesis, are activated by the catalyst. He thought it might be possible to connect catalytic activities and the quantitatively measurable chemical affinities between the catalyst and hydrogen and oxygen. Attempts to correlate catalytic activity and the ability of the metal to dissolve hydrogen did not materialize experimentally. He found, however, without exception, that if a metal has a greater affinity for oxygen than for hydrogen, that its catalytic activity was increased by pretreatment with hydrogen and vice-versa.³ He gives a series of elements arranged in the order of hydrogen affinities and oxygen affinities. The oxygen series was based on the heat of formation of the simplest oxide while the hydrogen series was based on the amount of hydrogen adsorbed by the metal. With alloys containing one rare metal, and one iron group metal, the catalytic efficiency, after pretreatment, was that predictable from the foregoing principle, with the exception of ruthenium-iron. Palladium-platinum was also an exception to the rule. From the point of view of the more important question of the absolute effectiveness of the catalyst, Remy distinguished the further factor of the relative ease of stable oxide formation as compared to the combination with hydrogen, those catalysts favoring the reaction to stable oxide being relatively inefficient. He makes the wrong assumption that this is necessarily proportional to the heat of formation of the oxide.

Special Points

According to Sabatier,⁴ nickel cannot be used for the hydrogenation of the oxides of carbon to alcohols because it is too good a hydrogenation catalyst, taking the substances on through to methane.

Bogandy and Polanyi⁵ find that hydrogen atoms are emitted when a jet of sodium vapor is directed against a film of sulphuric acid, kept at liquid air temperature in a high vacuum. Only hydrogen molecules come off when a film of ice is substituted for the sulphuric acid. They think the explanation sufficient that the heat of reaction is negative in the latter case, and positive in the former one.

According to Clark,⁶ radiation of the platinum catalyst, (used for the oxidation of sulphur dioxide) with X-rays, produced erratic changes in its activity.

Belenski⁷ has found that for the catalytic decomposition of potassium chlorate, the poorest catalysts are those which are easily oxidized.

¹ *Z. anorg. allgem. Chem.*, 157, 329 (1926). For experimental method see, Remy and Gönningen: *Z. anorg. allgem. Chem.*, 149, 283 (1925).

² *Ber.*, 49, 2369 (1916).

³ Compare the discussion of "films on catalysts."

⁴ *Compt. rend.*, 185, 17 (1927).

⁵ *Naturwissenschaften*, 14, 1205 (1926).

⁶ *Brit. J. Radiology*, 23, 112 (1927).

⁷ *Chem. Abs.*, 21, 2415 (1927).

Jabozynski and Rytel¹ have found a novel type of auto-catalysis. $\text{H}_2\text{S}_2\text{O}_8$ decomposed monomolecularly and reversibly with the formation of monatomic sulphur. After the reaction had proceeded a certain distance, aggregates of sulphur started to form, stopping the reverse reaction, with a net increase in reaction velocity.

According to Schlesinger and Malkina-Okun,² the halogen acids shift the equilibrium, in the formation and saponification of ethyl acetate, in proportion to their concentration, and simultaneously catalyze the reaction. The shift in equilibrium is allowable; but is not connected with the catalytic action.

Experiments of Richards and Loomis³ seem to indicate that high-frequency sound waves catalyze the iodine "clock" reaction, and others. Their method of investigation was a little unorthodox.

Thoren⁴ found a stepwise increase in the activity of nickel as the temperature was raised. The reactions investigated were: $\text{C}_2\text{H}_4 = \text{C}_2\text{H}_2$; $\text{C}_6\text{H}_6 + 3\text{H}_2 = \text{C}_6\text{H}_{12}$; $\text{O}_2 + \text{H}_2 = \text{H}_2\text{O}$. The actual percentage increase in activity at the various activation temperatures was not reproducible.

Adsorbed substances can move around on the surface,⁵ as well as evaporate without having moved. Constable,⁶ accordingly, points out that collisions between more or less freely moving molecules in the film can take place. He also points out that this effect is probably of no great importance in catalysis.

H. A. Taylor and Pickett⁷ find, in decomposing hydrogen sulphide on platinum by a streaming method, that there is a region where the rate of decomposition is independent of the rate of flow. The temperature coefficient at this stage was 11,750 calories. They conclude that this represents the heat of evaporation of sulphur from the surface. This does not seem a necessary conclusion.

Miscellaneous Results

Pearce and Ott⁸ decomposed various esters upon pumice-supported nickel. Added hydrogen was found not to change the reaction products.

Ottenssooser⁹ has found a zinc oxide catalyst effective for the oxidation of alcohols to aldehydes or ketones.

Uchida,¹⁰ has studied the catalytic decomposition of nitric oxide on platinum and on Fe_2O_3 , and says that this reaction affects the yield in the oxidation of ammonia by these catalysts.

Zelinski and Balandin¹¹ studied the dehydrogenation of decahydronaphthalene over various catalysts, and found the order of activity to be platinum-asbestos, platinum-charcoal, palladium-asbestos, nickel-asbestos.

¹ Chem. Abs., 21, 2415 (1927).

² Ber., 60, 1479 (1927).

³ J. Am. Chem. Soc., 49, 3086 (1927).

⁴ Z. anorg. allgem. Chem., 163, 367 (1927); 165, 171 (1927).

⁵ E.g. Becker: Phys. Rev., (2) 28, 341 (1926).

⁶ Proc. Cambridge Phil. Soc., 23, 593 (1927).

⁷ J. Phys. Chem., 31, 1212 (1927).

⁸ J. Phys. Chem., 31, 102 (1927).

⁹ Bull., 41, 324 (1927).

¹⁰ J. Soc. Chem. Ind., (Japan), 30, 171 (1927).

¹¹ Z. physik. Chem., 126, 267 (1927).

Madenwald, Henke, and Brown¹ studied the rate of hydrogenation of nitrobenzene on lead catalysts. The formation of azobenzene is a side reaction, the extent of which depends upon, (1) the metal constituting the catalyst, (2) the activity of the particular catalyst, (3) the temperature.

Lang² finds silver to catalyze the change of manganic to manganous chloride, and the evolution of chlorine from dilute hydrochloric solution by cerium nitrate.

Walker³ has conducted an extensive investigation of the reactions of ethylene over various catalysts. Various products of decomposition were identified. A polymerized oil was also found. He was unable to identify the active constituent of Jena glass by trying them out separately. He concluded that, "The activation of the ethylene by the walls of the reaction chamber is thought to be due to a combination of two or more of the oxide constituents, which come into play at the elevated temperature." Silica gel, silica gel and borax, silica gel and calcium hydroxide, calcium hydroxide, borax, calcium silicate, zinc oxide, ferric oxide, the oxides of lead, sodium, nickel, cobalt, iron, alkalized iron, chromium oxide-iron, and pumice-iron were investigated at various temperatures.

According to Palmer,⁴ the rate of reduction of copper oxide on clay by carbon monoxide is not governed by the rate of diffusion through the already reduced copper film, and the reduction is not hindered by the carbon dioxide formed. When hydrogen was the reducing agent, after a rapid initial reduction, the reaction came almost to a standstill. Water apparently poisons the reaction.

Only such results have been placed in this section as do not fit very well under the previous heads. No attempt has been made to exhaust the literature of the year (for instance, that of organic chemistry) with respect to miscellaneous results, desirable as that may have been for some purposes. The spirit of this report has been rather to systematize the results, and to try to enumerate and evaluate, as far as possible, the various factors which could be expected to operate in catalysis, which, after all, cannot be a new trick of nature entirely unrelated to the rest.

It is not universally realized that none of the work on catalysis has been, in a strict sense, quantitative. In no case has the number of reacting molecules upon the surface at a given time been known. In no case has the number of active catalyst atoms, or centers of a given type been accurately known. We have not been sure of the identity of the actual catalyst in many cases, nor of the reactants on the catalyst.

Some of these unknowns are starting-points for investigations of homogeneous reaction velocity. It is no wonder, then, that catalytic results are so often ambiguous and difficult to interpret.

January 23, 1928

¹ J. Phys. Chem., 31, 862 (1927).

² Ber., 60, 1389 (1927).

³ J. Phys. Chem., 31, 961 (1927).

⁴ Trans. Am. Electrochem. Soc., 51, 4 (1927).

THE ζ -POTENTIAL AND THE LYOTROPIC SERIES*

BY DAVID R. BRIGGS**

Investigations carried on in the many varied phases of colloid chemistry have, in general, given rise to the idea that colloid systems are subject to ionic influences which cannot be ascribed alone to the valence of the ions. It has been shown repeatedly that the stability of a colloid system is changed by different degrees when equivalent quantities of ions of equal valence are added to the system^{1, 2}. When comparative effects of neutral salts are determined upon such properties as the rate of inversion of cane sugar and other reaction velocities, upon the optical rotation of proteins in solution³, upon the solubility of non-electrolytes and peptization of colloids in water⁴, and upon the surface tension of aqueous systems, these are shown to be influenced by the series of ions in much the same order of sequence as is the stability of a colloid system.

That such a lyotropic series of ions exists has been denied by workers from time to time. Loeb⁵, from his work on the membrane potentials and their relation to viscosity, osmotic pressure, and other physical properties of protein solutions, concluded that the only differences demonstrable between salts of various ions could be entirely explained by differences in the valence of the ions being studied or by the changes, caused by the added salt, in the hydrogen ion concentration of the systems. ζ -potential measurements should be more apt to show these variations in the effects of ions on the electrical equilibrium in an interface than should the ϵ -potential (thermodynamic potential) which Loeb measured and called membrane potentials. This follows from the conception of Freundlich of the ζ -potential as existing across a movable and a fixed layer of the liquid phase in the immediate environment of the interface rather than across the actual interface. It would, therefore, show more readily changes in the liquid in this region which might not be pronounced enough to affect ϵ .

Pappadà⁶ was probably the first to point out that the coagulating power of monovalent ions is in the same order as their mobilities. The mobility of an ion is probably as important an indication of the reaction of that ion to its environment as is its valence, or its solubility. That the ions should show other properties which vary in intensity in the same order as their mobilities,

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¹ Krut: *Kolloid-Z.*, 22, 81 (1918).

² Freundlich and Ettisch: *Z. physik. Chem.*, 116, 401 (1925).

³ Carpenter: *J. Phys. Chem.*, 31, 1872 (1927).

⁴ Gortner, Hoffman, and Sinclair: *Kolloid-Z.*, 44, 97 (1928).

⁵ Loeb: "Proteins and the Theory of Colloidal Behavior" (1924).

⁶ Pappadà: *Kolloid-Z.*, 4, 56 (1909).

might be expected. Mukherjee⁷ derived a mathematical expression defining the electrical conditions in an interface at equilibrium. He equated the rate of evaporation of ions which are present in the interface phase to the rate of re-adsorption into this phase. His equation states that the number of ions forced into the interface in a given time is dependent (other things being equal) upon the speed of travel of the ions in an electric field, *i.e.*, the mobility of the ion. He failed to consider, however, that the number of ions moving out of the interface in the same time will also depend upon the speed of travel of the ions, *i.e.*, the diffusion mobility of the ions, and that this is equal to their electrical mobility. Since ions move with speeds proportional to their mobilities regardless of the nature of the force which is acting upon them, it seems unlikely that ionic mobility, as such, should play any part in determining the point at which equilibrium is attained between the interacting forces. This point will be defined by those forces alone; mobility of the ion will govern only the speed with which equilibrium may be attained.

When an ion is subjected to an electric field, it tends to move with a uniformly accelerated motion. Actually, however, the ion moves at a constant speed at equilibria such that the frictional forces of the medium are equal to the electrical forces tending to move the ion. Assuming that all ions of equal valence carry exactly equal electric charges, the speed with which they move will be a measure of the friction offered to their motion by the medium, which in turn is a measure of the attraction which the ion has for the molecules of the solvent, and which, in the case of a water medium, is known as the hydration capacity of the ion. The mobility of the ion, then, is a measure of the attraction which that ion has for the molecules of the surrounding liquid. This attraction is not a governing influence in determining the solubility of an ion (or its salt) in a medium, as might be expected. This is shown in Table I (data from Landolt-Börnstein: "Physikalisch-chemische Tabellen"):

TABLE I

| Ion | Mobilities | Solubilities of Chlorides at 0°C. | Ratio |
|-----------------|------------|--------------------------------------|-------|
| Li | 33.4 | 63.7 | .52 |
| Na | 43.5 | 35.7 | 1.22 |
| NH ₄ | 64.0 | 29.4 | 2.18 |
| K | 64.6 | 28.5 | 2.27 |
| Cs | 68.0 | 161.4 | .42 |
| H | 315.0 | 82.5 (10°C.) | 3.84 |

However, that mobility is a measure of a *real* attraction between the ions and the medium cannot be doubted. The mobility of an ion may change to a large degree with a change of medium, but the order of the mobilities of a series of ions remains about the same, since it seems to be a function of atomic weight (for simple equivalent ions). It may vary markedly, however, in the

⁷ Mukherjee: "Discussion on Colloids", Faraday Soc., p. 102, October (1920).

relative values. Table II shows the ionic mobilities of various monovalent anions and cations in H_2O and in NH_3 solutions, as given by Franklin and Cady⁸:

| Ion | In NH_3 | In H_2O | NH_3/H_2O | Ion | In NH_3 | In H_2O | NH_3/H_2O |
|----------|-----------|-----------|-------------|-----------|-----------|-----------|-------------|
| Li^+ | 112 | 33.3 | 3.36 | BrO_3^- | 148 | 47.6 | 3.11 |
| Ag^+ | 116 | 54.0 | 2.15 | NO_3^- | 171 | 61.8 | 2.77 |
| Na^+ | 130 | 43.4 | 3.00 | I^- | 171 | 66.6 | 2.57 |
| NH_4^+ | 131 | 64.7 | 2.03 | Br^- | 172 | 67.7 | 2.54 |
| K^+ | 168 | 64.5 | 2.61 | Cl^- | 179 | 65.5 | 2.73 |

The mobility of the cations, Li^+ , Na^+ , and K^+ , for instance, in NH_3 is still in the same order as in H_2O , but Li^+ carries relatively more current in NH_3 than in H_2O . The Ag^+ and NH_4^+ ions have a much lower relative mobility in NH_3 than in H_2O , due probably to the formation of a complex, heavy ion by the attraction of NH_3 molecules to these ions in a manner similar to hydration of Li^+ ion in H_2O . This tendency of an ion to attract molecules of its solvent might be called, for lack of a name, its lyophilicity, *i.e.*, its ability to attract its medium of dispersion. The lyophilicity of one phase toward another is an evidence of the tendency toward the formation of a quasi-chemical compound between them, in which not the primary but the secondary valencies⁹ of both phases play the important part.

The intermolecular forces which determine the lyophilicity that one substance will exhibit toward another substance are forces which help determine the adsorbability of one substance upon the surface of another. These forces, whether denoted as chemical or physical, are electrostatic in nature and will be explained ultimately in terms of the electron theory of atomic structure.

Similarities in molecular composition and structure of two compounds are known to indicate their mutual solubility. Molecules of the solute, in this case, dissolve in the solvent with the least possible distortion of the electrostatic conditions present therein. The limit of solubility is attained when the solution pressure is equalized by the osmotic pressure of the dissolved substance and the free energy of the system is at a minimum.

The lyophilicity that a substance may show toward the medium in which it is dispersed will not be so closely related to similarities in molecular structure (which picture primary valencies) as to the complimentary properties of their respective electrostatic spheres of influence or partial valencies. With our present incomplete knowledge of these forces which determine the properties of the atom, it is not possible to foretell definitely the lyophilicity of one material for another. The limit of lyophilicity will be attained when the kinetic motion of the molecules of the lyophilent (*i.e.*, dispersion medium) is just able to overcome the force of fixation or orientation at the surface of the disperse phase.

⁸ Franklin and Cady: *J. Am. Chem. Soc.*, 26, 499 (1904).

⁹ Secondary valence is used in the sense of Werner, and may be any electrostatic influence or orientation tendency.

The adsorbability of a substance on the surface of another substance is probably due to a tendency of the latter to act as a lyophilic for the former. If a substance forms a perfect solution in both phases of a two-phase system, it has no lyophilicity for either phase and distributes itself according to the Nernst distribution law, *i.e.*,

$$\Delta\bar{F} = RT \ln C_1/C_2 \quad (1)$$

and the ratio, C_1/C_2 , of the concentrations in the two phases is a constant. If the solute shows lyophilicity toward one phase, its activity in that phase is decreased (equivalent to an increase in its molecular weight) and the ratio ceases to be a constant, the solute tending to become more concentrated than would be expected in the phase toward which it shows lyophilicity. At low concentrations of the solute virtually all of the solute would accumulate in this phase. If this phase were the interface layer in contact with a solid adsorbent, its properties would be to a large extent determined by the electrostatic forces present on the surface of the solid, and we could think of the surface of the solid as constituting this phase. The solute will then, being lyophilic toward this phase, accumulate almost completely on the surface at low concentrations of the solution and, as this phase becomes more and more saturated toward the solute, the amount adsorbed will vary exponentially with the concentration of the solution, according to an equation such as:

$$\ln C_1 = \frac{\Delta\bar{F}}{RT} + x \ln C_2 \quad (2)$$

$$\text{or} \quad C_1 = C_2^x e^{\frac{\Delta\bar{F}}{RT}} \quad (2a)$$

where the value of x would be directly proportional to the lyophilicity forces acting on the solute in the surface phase. Adsorbability, then would be a function of the lyophilicity that a solute would show toward both the adsorbent and the solvent out of solution in which the adsorbed material is being taken.

Molecules have varying adsorbability due to structure and composition; so also must ions. It is through this difference in the adsorbability of ions that the so-called ζ -potential or adsorption potential arises at the interface between water and such chemically inert substances as cellulose. The OH^- ion present in H_2O is adsorbed preferentially to the H^+ ion due to its higher lyophilicity, we must suppose, in the cellulose surface phase or, if the cellulose is entirely inert, in the interface layer of the water. Harkins¹⁰ has emphasized the fact that these thin interfacial films are independent phases. The hydroxyl ion tends to penetrate this phase more deeply than does the H^+ ion but can move away from the H^+ ion only until the adsorptive or lyophilicity forces are equalized by the electric potential set up by such separation of the ions. Some H^+ ions will be dragged into the interior of the "solid" phase and the HOH thus dissolved in the solid will be water of hydration or adsorbed water. As the water of hydration increases in amount (which it should do

¹⁰ Harkins: Colloid Symposium Monograph, 5, 19-48 (1928).

with time as equilibrium is very slowly attained), the attraction that the interface phase has for the OH^- ion will decrease slightly and the ζ -potential will correspondingly decrease. This has been demonstrated to occur with sintered glass by Fairbrother and Varley¹¹ and has been observed with cellulose by the author.

The potential existing across the interface will in many cases be partly due to ions set free at the surface of the solid phase. The potential, however, will at all times be governed by all the ions present in the system and their relative lyophilicities in the two phases.

Just as the solubility equilibrium of a system is changed when a chemical reaction occurs between the phases, so will the adsorption equilibrium be changed when chemical reaction occurs between the adsorbent and the adsorbed material. Likewise the interface potential will be markedly changed in character, if such a chemical reaction occurs. For example, it is found that with a positively charged Al_2O_3 diaphragm the presence of the anions, Cl^- , Br^- , and I^- , in concentrations of .0001 N solution have a comparatively small effect upon the ζ -potential but when a .00005 N, or even more dilute, solution of the fluoride ion is forced through the diaphragm, the sign of the ζ -potential is totally reversed and the charge on the diaphragm is then found to be nearly as strongly negative as it was formerly positive. The explanation, of course, is that, due to the insolubility of the compound AlF_3 , the surface has been changed from Al_2O_3 [or $\text{Al}(\text{OH})_3$] to AlF_3 , and an excess of F^- ions have been adsorbed to give the originally positively charged surface (probably positively charged due to the going into solution of OH^- ions) a negative charge. Obviously, the effect of the F^- ion upon this interface is not a function of the interrelations of secondary valencies of the ion and solid (the lyophilicity of the ion toward the solid) but is due to the chemical reaction (primary valencies) taking place between solid and ion, plus the lyophilicity of the ion toward the new surface thus formed. Such a case as this must require a specific explanation and cannot fit into a general theory of ionic influences at interfaces.

A theory attempting to picture the influence of ions upon interface potentials must therefore deal with only those cases where the ions and the adsorbent do not react chemically, *i.e.*, where the attracting forces do not destroy the chemical individuality of the ion or alter the surface of the adsorbent. A study of ionic influences at the interface, cellulose-water, should be instructive, due to the chemical inertness of cellulose and the fact that it may be obtained virtually free from ash constituents which might prove troublesome.

Nernst showed that when a solute is added to a system of two immiscible solvents and its molecular weight is the same in both solvents, it will distribute itself in such a way that the ratio between the two concentrations is always a constant at constant temperature. Such a distribution is analogous to that of a substance between the liquid and gaseous phases and follows the same

¹¹ Fairbrother and Varley: J. Chem. Soc., 1927, 1584.

laws. When the solute is present in such a system in very small amounts so that it can be considered infinitely dilute, the fugacity of the solute in each phase is proportional to its mol fraction in that phase. At equilibrium its fugacities in both phases must be equal, and, therefore, as the amount of solute is varied, the mol fraction in one phase must remain proportional to that in the other phase¹², that is, for the solute in one phase $f_1 = k_1 N_1$ and in the other, $f_2 = k_2 N_2$. At equilibrium

$$\frac{f_1}{f_2} = \frac{k_1 N_1}{k_2 N_2} \quad \text{and} \quad \frac{N_1}{N_2} = \frac{k_1}{k_2} = \text{constant} \quad (3)$$

In solution the fugacity of the solute may be defined in terms of the partial molal-free energy, \bar{F} , as follows:

$$\bar{F} = RT \ln f + B, \quad (4)$$

where B is a constant at constant temperature.

Between two states of the solute at constant temperature,

$$\bar{F}_2 - \bar{F}_1 = RT \ln \frac{f_2}{f_1} \quad (4a)$$

where \bar{F}_2 is the partial molal-free energy of the solute in the phase in which the partial molal-free energy is highest (Phase 2).

When equilibrium has been reached and its fugacities in the two phases are equal, the equation becomes:

$$\bar{F}_2 - \bar{F}_1 = \Delta\bar{F} = RT \ln K \quad (5)$$

$$\text{or} \quad K = e^{\Delta\bar{F}/RT} \quad (5a)$$

where K is a ratio of the mol fraction of solute in Phase 2 to that in Phase 1.

The probability of a mol of the solute being found in a given volume of Phase 1, at equilibrium may be denoted by the factor, $1/K+1$; then the probability of it being found in Phase 2 will equal

$$1 - 1/K+1, \text{ or } 1 - 1/e^{\Delta\bar{F}/RT} + 1.$$

If we now consider a system consisting of a liquid in which an electrolyte is dissolved, we find that the ions of the electrolyte will tend to distribute themselves between the body of the liquid (Phase 1) and the surface layer (Phase 2) in accordance with the laws of the distribution of a solute in a two-phase system as noted above.

Across the interface between the body of the liquid and its surface layer there will exist a potential difference, the source of which, for present purposes, is immaterial. The difference in the free-energy content of a single ion of opposite charge to the charge on the surface layer when in Phase 1 and when in Phase 2 will equal the work done in moving it from the bulk of the liquid into the surface layer. This work, $\Delta\bar{F}_1$, will equal the product of the force of

¹² Lewis and Randall: "Thermodynamics" (1923).

attraction between the two oppositely charged bodies and the distance through which they are moved toward each other.

The electrostatic attraction between two oppositely charged bodies is equal to the product of their charges, E , divided by the square of their distance apart, r^2 , and by the dielectric constant, ϵ , of the medium lying between them.

$$A = \frac{E}{\epsilon r^2} \quad (6)$$

When a single ion of opposite charge to and approaching an interface is considered, the attracting force between it and a point charge on the surface layer will equal

$$E = n_1 n_2 e^2 \quad (7)$$

where n_1 and n_2 are the valencies, respectively, of the ion and the point charge on the surface layer, and $e = 4.77 \times 10^{-10}$, the charge carried by one electron (Millikan).

$$\text{Then} \quad A = \frac{n_1 n_2 e^2}{\epsilon r^2} \quad (8)$$

Langmuir¹³ from a comparison of the latent heat of evaporation and the energy required to change the distance between molecules of solids, was able to estimate the distance through which atomic forces are effective. He obtained a value equal to 0.6×10^{-8} cm. greater than the distance of zero attraction, as the distance between atoms at which the maximum attraction was exhibited. At distances greater than this the attraction decreased rapidly (perhaps as the fourth or fifth power of the distance) to insignificant values. At a distance greater than 2×10^{-8} cm. from the point of equilibrium, or zero attraction, the attraction again becomes infinitesimal.

That the ordinary laws of electrostatic attraction will hold through distances of molecular dimensions is open to doubt. However, considering that these laws of electrostatic attraction do hold under these circumstances and taking as the value for r , the distance between the charges, as equal to 2×10^{-8} cm. (the distance which Langmuir suggests as the greatest distance at which the attraction will be acting), the work, $\Delta \bar{F}_1$, done when the ion is moved into the interface will be

$$\Delta \bar{F}_1 = \frac{n_1 n_2 e^2}{\epsilon r} \quad (9)$$

The probability of an ion of opposite charge moving into the interface will be:

$$1 - \frac{1}{e^{\Delta \bar{F}_1/kT} + 1}$$

where k is the Boltzmann constant $= R/6.06 \times 10^{23} = 1.372 \times 10^{-16}$.

¹³ Langmuir: J. Am. Chem. Soc., 38, 2245 (1916).

TABLE III
Showing Probability of an Ion of Valence n_1 , moving into Interface
of Point Charge n_2

Values of $x = \frac{1}{e\Delta\bar{F}_1/kT + 1}$

$r = 2 \times 10^{-8}$ cm. $\epsilon = 81$
 $T = 300^\circ\text{K.}$ $k = 1.372 \times 10^{-16}$

| $n_2 = 1$ | $n_1 = 1$ | $n_1 = 2$ | $n_1 = 3$ |
|-----------|-----------|-----------|-----------|
| | .96820 | .99890 | .99999+ |

Table III shows that the chance which an isolated ion (of opposite charge to that carried by the interface layer) will have to move into the interface, will be extremely high even when the valencies of the ion and of the point charge are low. If ions of opposite charge to the interface layer alone were to be considered in the influence of electrolytes on adsorption (ζ) potentials, it is evident that even a small concentration of any electrolyte would suffice to totally discharge this potential. Experience disproves this hypothesis. The effect that an electrolyte has upon the adsorption potential is, therefore, not alone that of the ion of opposite charge but is the algebraic mean of the effects of all the ions in the system of which the interface is a part. The effect which any one of these ions may have, will depend (1) upon its valence (whether + or -, and whether mono-, di-, tri-, etc.); (2) upon its lyophilicity for the liquid solvent; and (3) upon its lyophilicity for the interfacial layer or the surface of the adsorbent, as the case may be. The first of these governing conditions is usually the most important but may be modified to a marked degree by either or both of the other two conditions. It is through the second and third of these factors that the lyotropic series finds its theoretical foundation and here too arises the parallelism between the mobility of an ion and its position in the lyotropic series. The mobility of an ion, as mentioned above, is a measure of the lyophilicity that the ion has for its solvent. Other things being equal, the greater the lyophilicity of an ion for its solvent (and, therefore, the lower its mobility) the less will be its tendency to move out of the liquid phase into the interface layer. If a series of monovalent cations and anions were studied in relation to their relative effects upon the ζ -potential at an interface toward which the water phase carried the positive charge, it might be expected that those cations which were most highly hydrated (having lowest mobilities) would show the least tendency to move out of the positively charged liquid and therefore have the least effect toward making the other phase positive, that is, the least effect on lowering the ζ -potential. Likewise those anions which were most highly hydrated would be least adsorbed into the interface and therefore could have the greatest effect toward making the water phase more negative, thus cutting down on the ζ -potential across the interphase boundary. Recently, Vosnesenskii and Astachov¹⁴, in their studies

¹⁴ S. A. Vosnesenskii and K. Astachov: *Z. physik. Chem.*, 128, 362-8 (1927).

on the thermodynamic potential at the interface of two immiscible liquids, reached the same conclusion with relation to the effects of various monovalent cations and anions on such potentials, as these just offered for the effects of a lyotropic series of ions upon the ζ -potential.

In the case of ionic effects on proteins, it has been pointed out that the sequence of a lyotropic series of ions is reversed when the charge on the particle is reversed. Kruyt¹⁵ explains this in terms of an oriented hydration theory, assuming the direction of orientation of the water molecules to be reversed when the charge on the particle is reversed, thus causing a reversal in the order of depth to which the hydrated ions will be able to penetrate toward the surface of the particle. By the above outlined picture this phenomenon can be explained as well by assuming that the ion which is most highly hydrated will always have the strongest tendency to remain in the aqueous phase of the system. When the water is positively charged to the protein, the most highly hydrated cation, for example, will have the least effect toward lowering the ζ -potential (or lowering the free surface energy of whatever form). When the water is negatively charged toward the protein, the most highly hydrated cation will have the most effect in lowering the ζ -potential, and thus the sequence of a lyotropic series will be reversed.

Experimental

The measurements of ion effects upon the ζ -potential of cellulose given in this paper have been made by the streaming potential method described recently by Briggs¹⁶. The equation for calculating ζ is given as follows:

$$\zeta = \frac{\kappa_s H}{P} \times \frac{4\pi\eta}{\epsilon} \quad (10)$$

where η = viscosity of the liquid, ϵ = its dielectric constant, H = the observed E.M.F. across the diaphragm at pressure, P , and κ_s = the specific conductivity of the liquid as it exists inside the pores of the diaphragm.

κ_s is calculated from measurements of the resistance across the diaphragm when the liquid is present, and from the cell constant of the diaphragm determined with a standard KCl solution of specific conductivity high enough to eliminate surface conductance effects when it is in the diaphragm. It is necessary to assume that the viscosity and dielectric constant of the very dilute solutions used in these experiments will not deviate appreciably from these values for pure water¹⁷. The value for ζ then will be proportional to the value for $H\kappa_s/P$, and it is this value which is plotted in Figs. 1-3.

The value of H is taken in millivolts, of P in cm. of Hg, and of κ_s in reciprocal ohms. H was measured by use of a Leeds and Northrup Type K potentiometer, using a quadrant electrometer, connected in series with the

¹⁵ Kruyt: "Colloids—A Textbook", translated by H. S. van Klooster, p. 237 (1927).

¹⁶ Briggs: J. Phys. Chem., 32, 641 (1928).

¹⁷ The technic for making the necessary measurements and a discussion of the necessary assumptions involved in the above formula have already been presented in detail in the early paper and will not be repeated here.

streaming potential cell, as a null instrument, thereby eliminating polarization effects. The accuracy with which the value H could be measured was to approximately 1 millivolt. Thus, when the value of H was high, the percentage error was lower than when H was low. For this reason P was always kept as high as practicable. When ζ approached a zero value, however, the percentage error was always greatest because of the low value of H .

It was found that a diaphragm which had been used with one salt could not always be thoroughly freed from that salt by washing, and if other salt solutions were brought in contact with this diaphragm, the values observed for ζ were prone to be more erratic than when a fresh diaphragm was used. For each new salt, then, a new diaphragm was used and the value of ζ for each diaphragm was determined against conductivity water (specific conductivity = approximately 2×10^{-6} mho) before the salt solutions were forced through it. Successively more concentrated solutions of the salt were then forced through the diaphragm and the value of ζ determined for each.

It has been shown that the value of ζ determined by this method is independent of the size of the pores in the diaphragm where a uniform sample of diaphragm material is used to form the various diaphragms. It has also been shown that different samples of cellulose vary in their ζ -potential against water. In the present experiments Schleicher and Schüll filter paper No. 589 was used for the diaphragm material. Due to difficulty encountered in thoroughly mixing the large quantity of paper needed for all the experiments made, thorough mixing was not attained and there was a resulting variation in the initial values of the ζ -potential shown by the different pulp preparations against water. An experiment with KCl upon diaphragms having different initial values of ζ against water showed that the effect of a given concentration of the ions upon the potential approximated the same percentage of the initial value of ζ , Table IV.

TABLE IV
Value of $\kappa_s H/P \cdot 10^5$ at Various Concentrations of KCl for Two Diaphragms of Different Initial Values of $\kappa_s H/P$ against Water

| | H ₂ O | .00005 N | .0001 N | .0002 N | .0004 N | .0008 N |
|-----|------------------|----------|---------|---------|---------|---------|
| A | 12.68 | 15.0 | 15.6 | 14.2 | 13.7 | 13.2 |
| B | 13.70 | 16.0 | 17.1 | 14.9 | 14.7 | 14.4 |
| B/A | 1.080 | 1.065 | 1.095 | 1.050 | 1.075 | 1.090 |

It was found that when the initial value of ζ (for the diaphragm against water) was very different, however, as, for example, when $\kappa_s H/P$ values were 12×10^{-5} and 18×10^{-5} , respectively, the variation in the percentage effect was too great to allow a reduction to a common scale for comparison. But when the initial value of $\kappa_s H/P$ did not vary more than approximately 1.5×10^{-5} (about 15%) from the mean value, it has been assumed that these values can be reduced to a common basis and compared. Table V gives the observed values of $\kappa_s H/P$ for the various solutions, while the curves shown are plotted from these tables after the values therein shown have been reduced

to a common basis, namely, for all initial values of the diaphragms against water the value $\kappa_s H/P$ has been equated to 10×10^{-5} and the corresponding values of $\kappa_s H/P$ for the salt solutions reduced to this basis.

TABLE V
Values for $\kappa_s H/P \cdot 10^5$ for Cellulose Diaphragms against Salt Solutions of Varying Concentrations

| Salt | H ₂ O | .00005 N | .0001 N | .0002 N | .0004 N | .0008 N | .0016 N |
|--------------------|------------------|----------|---------|---------|---------|---------|---------|
| KCl | 12.68 | 15.00 | 15.50 | 14.20 | 13.70 | 13.15 | 12.00 |
| NaCl | 12.27 | 14.58 | 16.15 | 15.30 | 14.35 | 12.65 | 11.40 |
| LiCl | 10.12 | 13.34 | 14.43 | 14.00 | 13.20 | 11.46 | 9.87 |
| CsCl | 10.11 | 11.75 | 12.25 | 10.90 | 10.54 | 10.14 | 8.78 |
| HCl | 11.94 | 9.72 | 8.89 | 7.89 | 6.38 | 5.26 | 3.30 |
| BaCl ₂ | 9.29 | 7.63 | 7.02 | 6.52 | 6.22 | 5.66 | 4.40 |
| SrCl ₂ | 10.90 | 9.32 | 8.50 | 8.13 | 8.45 | 8.45 | — |
| AlCl ₃ | 9.75 | 6.86 | 5.82 | 4.46 | 2.60 | 1.50 | 0.00 |
| ThCl ₄ | 12.70 | 3.80 | 0.71 | +2.40 | +7.06 | +10.60 | +12.20 |
| NH ₄ Cl | 15.35 | 17.60 | 17.90 | 16.70 | 15.20 | 13.45 | 13.30 |
| NH ₄ Ac | 13.60 | 14.28 | 14.41 | 13.22 | 12.40 | 10.82 | 9.36 |

Fig. 1 shows graphically these determinations where the values of $\kappa_s H/P$ are reduced to a common basis and are plotted against the concentration of the salt solutions. All the salts used were chlorides, so that the variations in effects shown were due to the cation part of the molecule. Salts of all the monovalent cations, except that of the H⁺ ion, showed an initial increase in the ζ -potential up to a concentration equal to .0001 N with a subsequent slow decrease. The hydrogen ion showed a greater effect toward reducing the ζ -potential than did di-valent cations. Reversal of the charge was obtained only with the tetra-valent cation, Th⁺⁺⁺⁺, though with some samples of cellulose the Al⁺⁺⁺ ion has been found to bring about a slight reversal of charge.

Those ions which most strongly affect the charge, *i.e.*, Th, Al, and H, are found to do so in such a manner that the values, when plotted, form a near approximation to a straight line when the $\kappa_s H/P$ value is plotted against the log concentration values, as in Fig. 2. An equation for these curves will therefore take the form,

$$\log c = \log a + \frac{\kappa_s H}{P} b \log e \quad (11)$$

$$\text{or} \quad c = a e^{b \frac{\kappa_s H}{P}} \quad (11a)$$

While the values for c_1 in these curves, denotes the concentration of the salt in the solution at equilibrium, this concentration bears a constant ratio to the concentration of the salt in the interface layer when the Nernst distribution law holds. The value $\kappa_0 H/P$ multiplied by a constant (1.0596×10^6)

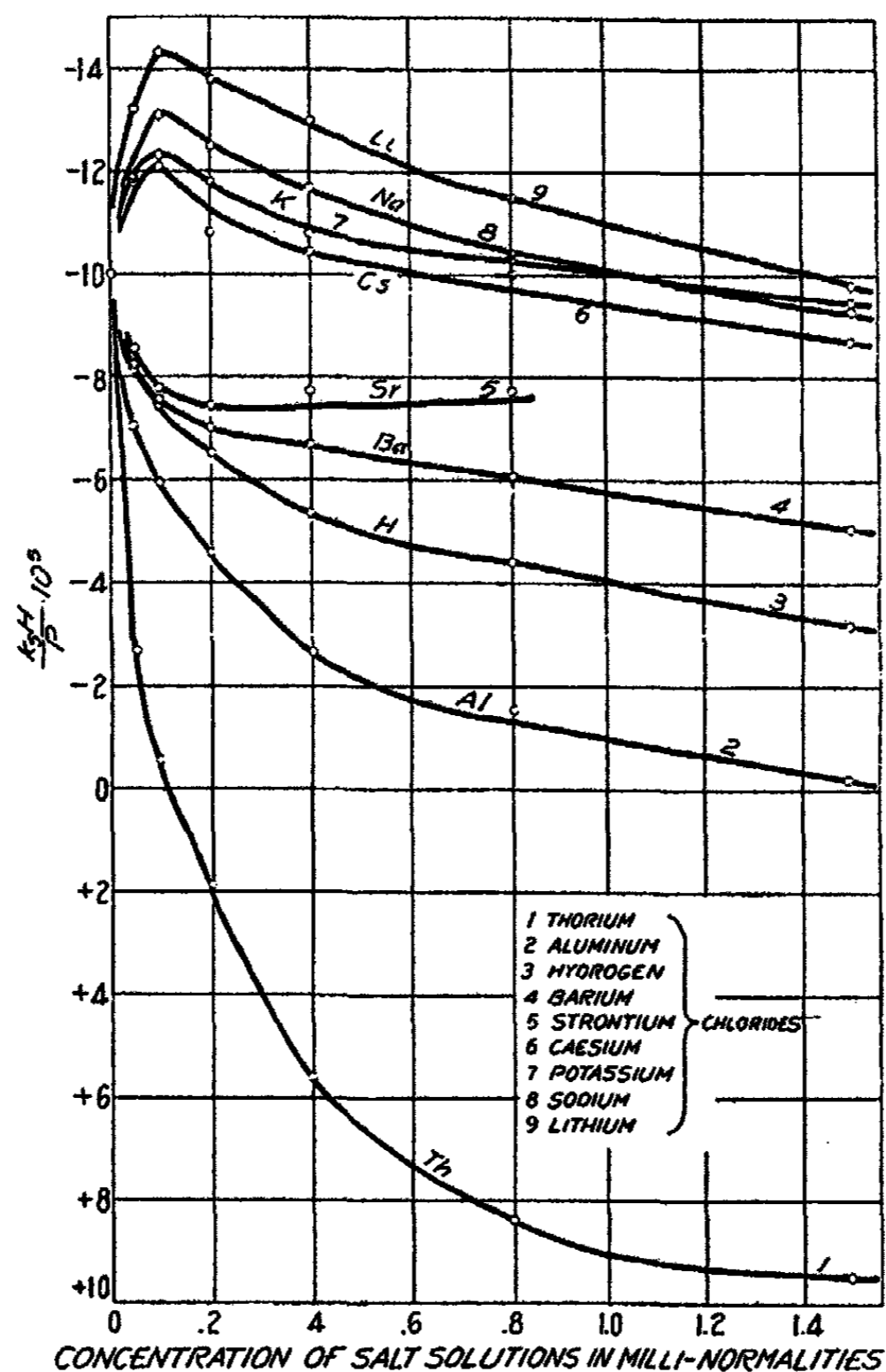


FIG. 1

Influence of cation chlorides upon the ζ -potential at cellulose-water interface.

Vertical axis = $\frac{\kappa_0 H}{P} \cdot 10^6$.

Horizontal axis = concentration of salt solutions in milli-normalities.

gives the corresponding value for the ζ -potential, which is a measure of one form of free surface energy. When the free energy of a phase varies with the amount of some solute present therein, an expression of the partial molal free

energy content, \bar{F} , of the solute in this phase at any concentration, c , of the solute is given by the equation,

$$\bar{F} = RT \ln c + B \quad (12)$$

where B is some constant depending only on the temperature; or at constant temperature

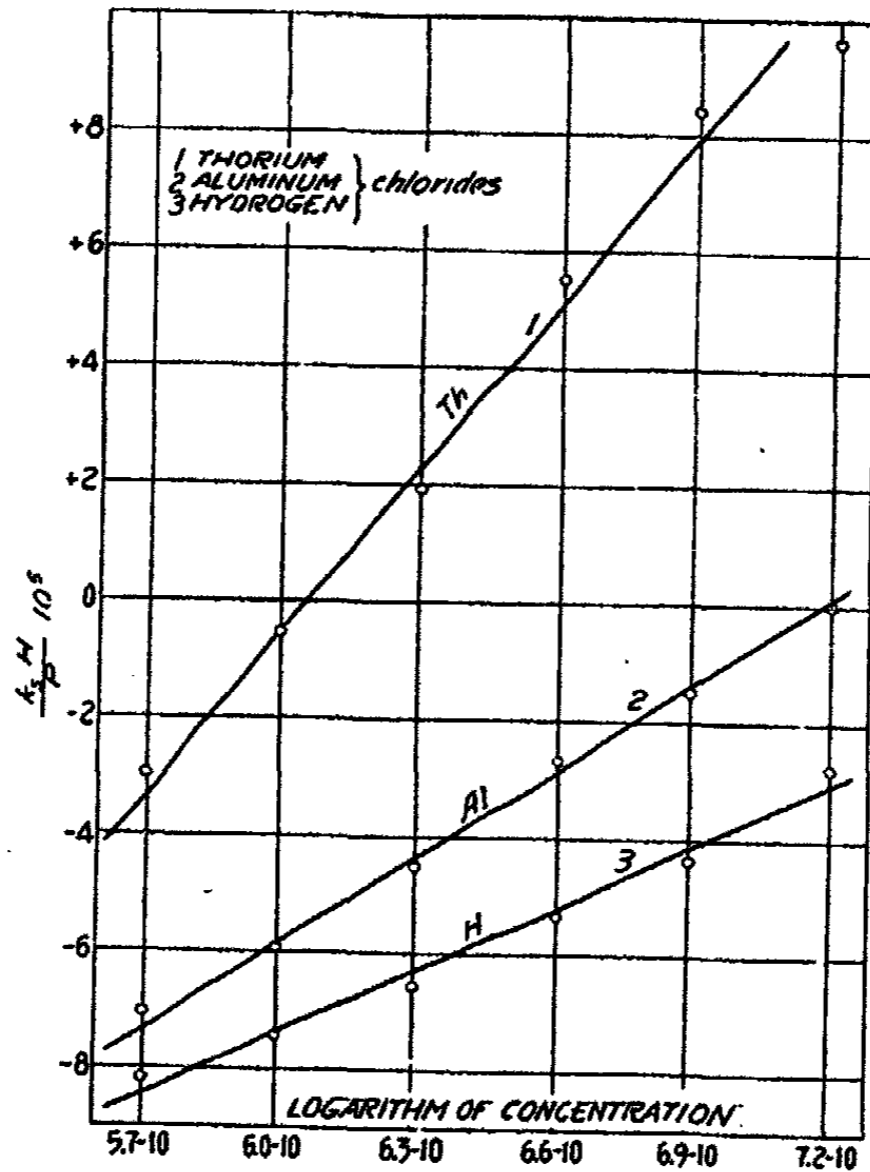


FIG. 2

Influence of cation chloride upon ζ -potential at cellulose-water interface.

Vertical axis = $\frac{\zeta H}{P} \cdot 10^5$.

Horizontal axis = logarithm of concentration of salt solutions in normalities.

$$c = e^{\frac{1}{RT} \cdot \bar{F}} \quad (12a)$$

The parallelism between these equations and the terms thereof, indicates that the ζ -potential-concentration relationship is a function of the relationship of the partial molal free energy of the salt present in the surface layer to its concentration in this layer.

Fig. 3 compares the effects of two anions, Cl^- and Ac^- , of equal valence but different mobilities, upon the ζ -potential at the cellulose-water interface.

It would seem that, in the case of the monovalent cation chlorides, the curves are the resultant of two concentration-free energy curves. The one more pronounced at lower concentrations is that due to the preferential adsorption of chloride ions, this being over-shadowed and neutralized at higher concentrations by that due to the cation part of the molecule.

Discussion of Results

It is evident from these data that the effect which a salt solution has upon the ζ -potential is a function not alone of the ion carrying the opposite charge to that of the colloid but of all the ions present in the system and to which the

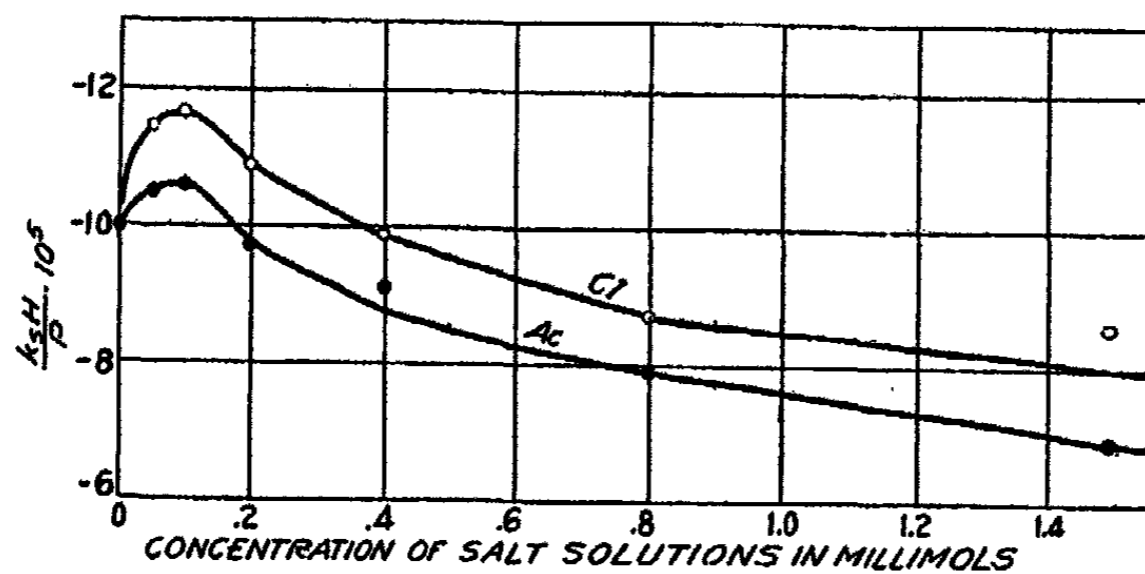


FIG. 3

Influence of anions of ammonium salts upon the ζ -potential at cellulose-water interface.

Vertical axis = $\frac{k_s H}{P} \cdot 10^5$.

Horizontal axis = concentration of salt solutions in millimols.

interface is accessible. In the case of a cellulose-water interface, and of all water interfaces toward inert materials, the hydroxyl ion seems to have a higher lyophilicity in the interface layer than does the hydrogen ion and moves into this interface phase, causing it to assume a negative charge toward the bulk of the liquid. The same thing must be true of the Cl^- ion to perhaps an even greater extent since, with all salts with monovalent cations, it causes an initial increase of the ζ -potential, which is gradually, though never completely, discharged as the concentration of the salt becomes greater. This discharging effect may be entirely due to the decrease in the distance into the solution to which the potential difference extends, by the increase in salt concentration in the solution, thus cutting down on the potential difference which exists across the movable-immovable layer, *i.e.*, the ζ -potential (See Freundlich¹⁸). The ϵ -potential, or thermodynamic potential, arises from the same source as the ζ -potential, *i.e.*, the unequal distribution of ions across the interface, but it does not necessarily vary in the same manner as does the ζ -potential.

If we picture the original potential at the water-cellulose interface as due to an unequal distribution of OH^- and H^+ between the phases, it is to be

¹⁸ Freundlich: "Colloid and Capillary Chemistry", (1926).

expected that polyvalent ions will greatly lower the ζ -potential because one such ion can take the place of two, three, or four H^+ ions in the environment of the interface. Since the kinetic energy content of one H^+ ion is equal to that of one Al^{+++} ion, when one Al^{+++} ion has replaced three H^+ ions in the environment of the interface, it is evident that the Al^{+++} will reach a position of equilibrium at a point much deeper in toward the interface layer than that previously occupied by the three H^+ ions, and that the ζ -potential will be accordingly smaller.

Among ions of equal valence, the depth to which these will penetrate in toward the interface phase will depend upon their lyophilicity for the various phases of the system. Other things being equal, the higher the mobility (lower the hydration) of an ion, the deeper will it penetrate toward the interface phase before attaining equilibrium. When the water carries the positive charge, as at the interface under discussion, the more highly hydrated a cation may be, the less tendency will it have toward discharging the ζ -potential. This is well illustrated in the data already presented. Lithium, sodium, potassium, caesium, and hydrogen have respectively greater effects toward discharging the ζ -potential, and they are respectively less hydrated, or less lyophilic toward water. With anions at the same interface, the greater the hydration the greater should be the discharging effect (because the greater would be the tendency for the negatively charged ion to remain in the positively charged phase). This is illustrated in the case of the Cl^- and Ac^- ions. The acetate ion is more highly hydrated than is the Cl^- ion (mobilities are 35 and 65.5, respectively), and the acetate ion tends to discharge the ζ -potential to a greater degree than the Cl^- ion (Fig. 3) at a given concentration.

Electrical potential difference is a variable dependent upon other conditions of energy distribution in the interface layer and is probably of secondary importance. The curve for the effect of the Th^{++++} ion on the ζ -potential at the water-cellulose interface indicates that the electrical free energy at the interface is not the only form of free surface energy which is being acted upon by the adsorbed salt but may be only secondary to some other free surface energy change which is taking place at the same time. This is evidenced by the fact that the Th^{++++} not only reduces the ζ -potential to zero, but the rate of change in the potential charge at the interface does not alter at the zero point but rapidly increases again on the positive side at very low concentrations of Th^{++++} , thus building up again the electric free surface energy (but of opposite sign) at the interface.

At an interface between two phases there is always present a condition of strain, due to unsaturation of partial valence forces. A part of this free energy of the surface zone will usually be manifested by the presence of an electrical potential difference. This potential arises from the fact that, when a pair of ions, one plus, the other minus in charge, are brought into the interface region, one will nearly always show a greater tendency to lower the free energy of the surface layer than the other and will therefore be forced into that layer with more force than its mate. We can picture a condition in which one of a pair

of ions would tend to lower the surface energy to a large extent, whereas its mate would, if brought into the surface layer, cause an increase in the surface energy. In such a case, the former would move into the surface layer, while the latter would not and, while the surface energy as a whole would be lowered, a large electrical potential difference across the phase boundary would at the same time be formed. If both ions had about the same effect upon the surface free energy, either to decrease it or increase it, they would be equally attracted to or repelled from the surface layer and no change would occur in the electric potential present there.

The magnitude of the ζ -potential at an interface, therefore, does not necessarily parallel in value the adsorption capacity of that interface. It is only one of the forms in which free surface energy may be present and is, therefore, no more important than is surface tension, or any other condition of strain in which the surface energy may be able to exist, in defining the free energy content of the interface phase of a system. In order to completely define the conditions in the interface, the magnitude of all forms in which surface energy can exist must be determined. Adsorption of some substance may take place to a large degree without appreciably altering the magnitude of some forms of free surface energy. For example, it is conceivable that the free energy as exhibited by interfacial tension may be lowered out of all proportion to any corresponding change in the free surface energy represented by the electrokinetic potential. Other substances may affect all forms of the energy when they are adsorbed. Some substances may be adsorbed to cause a decrease in the total free energy of the surface layer, but at the same time increase the amount of free surface energy existing in some particular form.

In the case of thorium chloride, we may assume that the total free surface energy is decreased with increased concentrations. The electrical free energy of the surface layer, however, is first decreased to zero and then increased in the opposite direction, showing that the thorium ion had been strongly oriented toward the surface layer even after the charge had been reversed and, while the total free surface energy is being lowered with increased concentration, the electrical free surface energy is being increased. At still higher concentrations of thorium chloride, it has been found that the ζ -potential is lowered toward zero again by the increased effect that the Cl^- ion has at these higher concentrations. This effect is confirmed by the earlier experiments of Kruyt¹ in the case of Al^{+++} and glass.

Conclusion and Summary

1. Series of ions are shown to affect the ζ -potential at an inert interface (cellulose-water) in the orders of their mobilities. These mobilities are inverse measures of the lyophilicity (medium-loving) capacities of these ions in water. It is from this relative lyophilicity of ions for the phases of the system in which they are distributed that the ζ -potential arises and it is in this property of the ions that the lyotropic effect of ions has its theoretical foundation.

2. The effect that a salt solution has upon the ζ -potential is a function, not alone of the ion carrying the opposite charge to that of the colloid, but of all ions present in the system and to which the interface is accessible.

3. The ζ -potential is shown to vary with the concentration of the salt solution in the same manner as the variation of the partial molal free energy of a substance dissolved in a solvent varies with its concentration in that solvent,

$$c = a e^{b\zeta}$$

$$\text{and } c = e^{\bar{F}/RT}$$

being the equations defining these similar phenomena.

4. The change in the ζ -potential with ion concentration is, in some cases at least, secondary to other free surface energy changes and not, in itself, the determining factor in the adsorption phenomenon.

**OXIDATION OF FATS, NITROGENOUS SUBSTANCES, AND THEIR
MIXTURES WITH CARBOHYDRATES BY AIR, AND METAB-
OLISM IN NORMAL HEALTH AND DIABETES**

BY C. C. PALIT AND N. R. DEAR

In previous papers¹ published from these laboratories, we have investigated the oxidation of carbohydrates by passing air under different conditions. From our researches on the oxidation of carbohydrates, we have been able to explain the metabolism in different forms of diabetes, glycosuria, etc.

We have also proved experimentally that uric acid can be oxidised by passing air in presence of dilute solutions of caustic soda. Moreover, uric acid has been oxidised in neutral solutions by passing air in presence of ferrous hydroxide, manganous hydroxide, cerous hydroxide, cobaltous hydroxide, nickelous hydroxide, cupric hydroxide and sodium sulphite.

In this paper, we shall present the experimental results obtained in the slow oxidation of other nitrogenous products, fats, and carbohydrates, either occurring singly or as a mixture of two or three of these substances. The experimental arrangement and the method of estimation of various substances were the same as given in previous papers.

The experimental results given in Tables I and II show that, in presence of caustic soda or sodium bicarbonate, potassium stearate and potassium oleate are appreciably oxidised by passing air at the ordinary temperature in absence of any catalyst. Moreover, our experimental results show that in presence of caustic soda, there is more oxidation than in presence of sodium bicarbonate. In presence of the hydroxides of the different metals, the amount of oxidation of potassium stearate and potassium oleate is increased and the order of the accelerating effect is the following:—

Cerous hydroxide } manganous hydroxide } uranous hydroxide, cupric
hydroxide, ferrous hydroxide } nickelous hydroxide } ferric hydroxide } mer-
curic hydroxide, cobaltous hydroxide } lead hydroxide } chromic hydroxide
with potassium stearate and uranous hydroxide } cerous hydroxide } mer-
curic hydroxide } ferrous hydroxide } manganous hydroxide } ferric hydrox-
ide } cupric hydroxide } chromic hydroxide } lead hydroxide } nickelous hy-
droxide } cobaltous hydroxide with potassium oleate.

With hippuric acid and glycine, we observe from Tables VI-XIII, that these substances can be oxidised by passing air at the ordinary temperature in presence of alkali and in presence of different reducing agents, the amount of oxidation is increased.

¹ J. Phys. Chem., 29, 376, 799 (1925); 30, 939 (1926).

TABLE I
Potassium Stearate

Estimation of potassium stearate in presence of freshly precipitated hydroxides of different metals, caustic soda, sodium bicarbonate or sodium sulphite, in neutral and alkaline solutions. The volume of fat taken was 10 c.c. and the volumes of different salt solutions, each of 1.0% concentration were 20 c.c. in each case. The hydroxides were precipitated from the salt solutions by the addition of the exact equivalent amount of caustic soda. The volume of air passed was 60 litres in 9 hours.

| No. of Experiment | Substance (freshly precipitated hydroxides, caustic soda, sodium bicarbonate, or sodium sulphite) used as catalyst in the experiment | Volume of N/10 sodium thiosulphate required for 10 c.c. of iodine trichloride taken with 10 c.c. of fat after 2 hrs. (Blank) | Volume of N/10 sodium thiosulphate required for iodine trichloride left after the experiment in c.c. | Amount of fat oxidized in terms of N/10 sodium oxidised thiosulphate in c.c. | Percentage amount of fat oxidised |
|-------------------|--------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------|-----------------------------------|
|-------------------|--------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------|-----------------------------------|

A.—Neutral Solutions

| | | | | | |
|----|-----------------------------------------------|-----------|------|-----|------|
| 1 | Ferrous hydroxide | 14.2 c.c. | 17.9 | 3.7 | 63.8 |
| 2 | Ferric hydroxide | " | 17.6 | 3.4 | 58.6 |
| 3 | Cerous hydroxide | " | 18.2 | 4.0 | 68.9 |
| 4 | Chromic hydroxide | " | 17.2 | 3.0 | 51.7 |
| 5 | Cobaltous hydroxide | " | 17.4 | 3.2 | 55.1 |
| 6 | Nickelous hydroxide | " | 17.7 | 3.5 | 60.3 |
| 7 | Lead hydroxide | " | 17.3 | 3.1 | 53.4 |
| 8 | Mercuric hydroxide (wet HgO) | " | 17.4 | 3.2 | 55.1 |
| 9 | Manganous hydroxide | " | 18.0 | 3.8 | 65.5 |
| 10 | Uranous hydroxide | " | 17.9 | 3.7 | 63.8 |
| 11 | Cupric hydroxide | " | 17.9 | 3.7 | 63.8 |
| 12 | Sodium sulphite (=0.1513 gm.) | " | 15.0 | 0.8 | 13.7 |
| 13 | Sodium bicarbonate (= 10 c.c. of 1.0% sol'n.) | " | 17.4 | 3.2 | 55.1 |
| 14 | Caustic soda (= 10 c.c. of N/8 sol'n.) | " | 17.7 | 3.5 | 60.3 |

B.—Alkaline Solutions (= 10 c.c. of N/8 NaOH)

| | | | | | |
|----|-------------------------------|-----------|------|-----|------|
| 1 | Ferrous hydroxide | 14.2 c.c. | 18.1 | 3.8 | 65.5 |
| 2 | Ferric hydroxide | " | 17.9 | 3.7 | 63.8 |
| 3 | Cerous hydroxide | " | 18.5 | 4.3 | 74.1 |
| 4 | Chromic hydroxide | " | 17.5 | 3.3 | 56.8 |
| 5 | Cobaltous hydroxide | " | 17.6 | 3.4 | 58.6 |
| 6 | Nickelous hydroxide | " | 18.0 | 3.8 | 65.5 |
| 7 | Lead hydroxide | " | 17.5 | 3.3 | 56.8 |
| 8 | Mercuric hydroxide (wet HgO) | " | 17.8 | 3.6 | 62.0 |
| 9 | Manganous hydroxide | " | 18.2 | 4.0 | 68.9 |
| 10 | Uranous hydroxide | " | 18.1 | 3.9 | 67.2 |
| 11 | Cupric hydroxide | " | 18.0 | 3.8 | 65.5 |
| 12 | Sodium sulphite (=0.1513 gm.) | " | 15.1 | 0.9 | 15.5 |

10 c.c. of $\text{ICl}_3 + \text{KI} \equiv 20.0$ c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$.)

10 c.c. of potassium stearate + 10 c.c. $\text{ICl}_3 \equiv 14.2$ c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$.)

TABLE II
Potassium Oleate

Estimation of potassium oleate in presence of (i) freshly precipitated hydroxides of different metals in neutral solutions, (ii) caustic soda, sodium bicarbonate and sodium sulphite. The volume of fat used was 10 c.c. and the volumes of different salt solutions, each of 1.0% concentration, were 20 c.c. in each case. The hydroxides were precipitated from the salt solutions by the addition of the exact equivalent amount of caustic soda. The volume of air passed was 60 liters in 9 hours. (10 c.c. $\text{ICl}_3 + \text{KI} \equiv 17.4$ c.c. of $\text{N}/10 \text{Na}_2\text{S}_2\text{O}_3$.)

| No. of Experiment | Substance (freshly precipitated hydroxides, caustic soda, sodium bicarbonate or sodium sulphite) used in the experiment as catalyst | Volume of N/10 sodium thiosulphate required for 10 c.c. of iodine trichloride taken with 10 c.c. of fat after 2 hrs. (Blank) | Volume of N/10 sodium thiosulphate required for iodine trichloride left after the experiment in c.c. | Amount of fat oxidised in terms of N/10 sodium thiosulphate in c.c. | Percentage amount of fat oxidised |
|-------------------|-------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------|-----------------------------------|
| 1 | Ferrous hydroxide | 10.8 c.c. | 13.9 | 3.1 | 47.0 |
| 2 | Ferric hydroxide | " | 12.6 | 1.8 | 27.3 |
| 3 | Cerous hydroxide | " | 14.5 | 3.7 | 56.1 |
| 4 | Chromic hydroxide | " | 11.2 | 0.4 | 6.1 |
| 5 | Cobaltous hydroxide | " | 10.8 | 0.9 | 0.0 |
| 6 | Nickelous hydroxide | " | 10.9 | 0.1 | 1.5 |
| 7 | Lead hydroxide | " | 11.1 | 0.3 | 4.5 |
| 8 | Mercuric hydroxide (wet HgO) | " | 14.1 | 3.3 | 50.0 |
| 9 | Manganous hydroxide | " | 13.8 | 3.0 | 45.4 |
| 10 | Uranous hydroxide | " | 15.0 | 4.2 | 63.6 |
| 11 | Cupric hydroxide | " | 11.5 | 0.7 | 10.6 |
| 12 | Sodium sulphite (= 0.1513 gm.) | " | 12.3 | 1.5 | 22.7 |
| 13 | Sodium bicarbonate (= 10 c.c. of 1.0% sol'n.) | " | 11.9 | 1.1 | 16.6 |
| 14 | Caustic soda (= 10 c.c. of N/8 sol'n.) | " | 13.8 | 3.0 | 45.4 |

10 c.c. potassium oleate + 10 c.c. $\text{ICl}_3 \equiv 10.8$ c.c. of $\text{N}/10 \text{Na}_2\text{S}_2\text{O}_3$.

From our experimental results on the oxidation of the mixture of carbohydrates and fats as given in Tables III-V, XIV, XV, we find that both the carbohydrates and fats are oxidised by passing air at the ordinary temperature and the greater the amount of alkali, the greater is the amount of oxidation. Moreover, we have observed that a mixture of potassium stearate and

different carbohydrates or a mixture of potassium oleate and different carbohydrates can be oxidised by passing air at the ordinary temperature, though we have observed that solutions of carbohydrates cannot be oxidised in absence of alkali by passing air. The oxidation of carbohydrates in presence of potassium stearate or potassium oleate must be due to the existence of a small quantity of alkali obtained by the hydrolysis of potassium stearate or potassium oleate. It has also been observed that in presence of ferrous hydroxide or cerous hydroxide, the amount of oxidation of potassium stearate or potassium oleate and carbohydrates from a mixture of these substances is greatly increased.

From our experimental results given in Tables XIVB and XIVC, we find that by passing air for 9 hours, the amount of oxidation of starch, cane sugar, and glucose and other sugars from a mixture of each of these substances and potassium stearate is the following:—

| | | | |
|------------|------|------------|-------|
| Glucose | 9.5% | Starch | 41.3% |
| Cane sugar | 9.1% | Maltose | 21.5% |
| Starch | 21% | Lactose | 14.4% |
| | | Laevulose | 11.5% |
| | | Arabinose | 3.5% |
| | | Cane sugar | 10.5% |
| | | Galactose | 10% |

TABLE III

Estimation of potassium oleate in presence of freshly precipitated hydroxides of different metals and glucose occurring together in neutral solutions. The volume of air passed was 60 litres in 9 hours. (10 c.c. of $\text{ICl}_3 + \text{KI} \equiv 17.4$ c.c. of $\text{N}/10 \text{Na}_2\text{S}_2\text{O}_3$; 10 c.c. of potassium oleate $\equiv 10.8$ c.c. of $\text{N}/10 \text{Na}_2\text{S}_2\text{O}_3$ and 10 c.c. of glucose $\equiv 15.6$ c.c. of $\text{N}/10 \text{Na}_2\text{S}_2\text{O}_3$)

| No. of Experiment | Substance (freshly precipitated hydroxides) used in the experiment as catalyst | Volume of $\text{N}/10$ sodium thiosulphate required for 10 c.c. of iodine trichloride taken with 10 c.c. of fat after 2 hrs. (Blank) | Volume of $\text{N}/10$ sodium thiosulphate required for 10 c.c. of iodine trichloride taken with 10 c.c. of glucose after 2 hrs. (Blank) | Volume of $\text{N}/10$ sodium thiosulphate required for iodine trichloride left after the experiment in c.c. | Percentage amount of fat oxidised |
|-------------------|--------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|-----------------------------------|
| 1 | Ferrous hydroxide | 10.8 c.c. | 15.6 c.c. | 10.5 | 22.7 |
| 2 | Ferric hydroxide | " | " | 10.5 | 22.7 |
| 3 | Cerous hydroxide | " | " | 12.3 | 50.0 |
| 4 | Chromic hydroxide | " | " | 9.3 | 3.0 |
| 5 | Colbaltous hydroxide | " | " | 9.0 | 0.0 |
| 6 | Nickelous hydroxide | " | " | 9.0 | 0.0 |
| 7 | Mercuric hydroxide (wet HgO) | " | " | 11.8 | 42.4 |
| 8 | Manganous hydroxide | " | " | 11.6 | 39.3 |
| 9 | Uranous hydroxide | " | " | 12.7 | 56.0 |

10 c.c. potassium oleate + 10 c.c. $\text{ICl}_3 \equiv 10.8$ c.c. of $\text{N}/10 \text{Na}_2\text{S}_2\text{O}_3$.

TABLE IV
 Potassium Stearate

Estimation of potassium stearate in presence of (i) freshly precipitated ferrous hydroxide (= 0.0674 gm.), glucose or urea and (ii) freshly precipitated cerous hydroxide (= 0.0169 gm.) occurring singly or as a mixture of two or three of these substances. The volume of air passed was 60 litres in 9 hours. The volume of each of the solutions taken was 10 c.c. in each case.

| No. of Experiment | Substance or mixture of substances used in the experiment as catalyst | Volume of N/10 sodium thiosulphate required for 10 c.c. of iodine trichloride taken with 10 c.c. of fat after 2 hours. (Blank) | | A.—Neutral Solution | | B.—Alkaline Solution (Alkali = 10 c.c. of N/8) | |
|-------------------|-----------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|-----------------------------------|------------------------------------------------------------------------------------------------------|------------------------------------------------|------|
| | | Volume of N/10 sodium thiosulphate required for 10 c.c. of iodine trichloride taken with 10 c.c. of glucose or urea after 2 hours. (Blank) | Volume of N/10 sodium thiosulphate required for 10 c.c. of iodine trichloride left after the experiment in c.c. | Percentage amount of fat oxidised | Volume of N/10 sodium thiosulphate required for iodine trichloride left after the experiment in c.c. | Percentage amount of fat oxidised | |
| 1 | Glucose | 14.2 c.c. | 15.6 c.c. | 14.5 | 39.6 | 14.8 | 44.8 |
| 2 | Urea | " | " | 14.3 | 36.2 | 14.3 | 36.2 |
| 3 | Ferrous hydroxide | " | " | 17.9 | 63.8 | 18.1 | 65.5 |
| 4 | Ferrous hydroxide and glucose | " | " | 15.4 | 55.1 | — | — |
| 5 | Ferrous hydroxide and urea | " | " | 15.1 | 50.0 | 15.3 | 53.4 |
| 6 | Ferrous hydroxide and glucose and urea | " | " | 12.6 | 41.3 | — | — |
| 7 | Cerous hydroxide | " | " | 18.2 | 68.9 | 18.5 | 74.1 |
| 8 | Cerous hydroxide and glucose | " | " | 15.6 | 58.6 | — | — |
| 9 | Cerous hydroxide and urea | " | " | 15.5 | 56.8 | 15.7 | 60.3 |
| 10 | Cerous hydroxide and glucose and urea | " | " | 12.8 | 44.8 | — | — |

10 c.c. of $\text{ICl}_3 + \text{KI} \equiv 20.0$ c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$.

10 c.c. of potassium stearate + 10 c.c. of $\text{ICl}_3 \equiv 14.2$ c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$.

10 c.c. of glucose + 10 c.c. $\text{ICl}_3 \equiv 15.6$ c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$.

10 c.c. of urea + 10 c.c. $\text{ICl}_3 \equiv 15.6$ c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$.

10 c.c. $\text{ICl}_3 + \text{KI} \equiv 17.4$ c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$.

Whilst the amount of carbohydrates oxidised in absence of fat under otherwise identical conditions in $5\frac{1}{2}$ hours is the following:—(Vide Table IX A)

| | | | |
|------------|-------|------------|-------|
| Glucose | 11.4% | Starch | 49% |
| Cane sugar | 12.9% | Maltose | 31% |
| Starch | 30% | Lactose | 16.5% |
| | | Laevulose | 17% |
| | | Arabinose | 4% |
| | | Cane sugar | 21% |
| | | Galactose | 12% |

Consequently these results prove conclusively that the amount of oxidation of carbohydrates is greatly decreased by the presence of fats. Moreover from our experimental results given in Tables III-V, we note that the amount of oxidation of fats in a definite time is greatly reduced by the presence of carbohydrates. Hence we are convinced that the presence of fat or carbohydrate which is itself undergoing oxidation retards the oxidation of the other. Moreover from our experimental results it will be seen that in presence of carbo-

TABLE V
Potassium Oleate

Estimation of potassium oleate in presence of freshly precipitated ferrous hydroxide (= 0.0674 grm.) glucose or urea occurring singly or as a mixture of two or three of these substances. The volume of air passed was 60 litres in 9 hours. The volume of each of the solutions taken was 10 c.c. in each case.

| No. of Experiment | Substance or mixture of substances used in the experiment as catalyst | Volume of N/10 sodium thiosulphate required for 10 c.c. of iodine trichloride taken with 10 c.c. of fat after 2 hrs. (Blank) | Volume of N/10 sodium thiosulphate required for 10 c.c. of iodine trichloride taken with 10 c.c. of glucose or urea after 2 hrs. (Blank) | Volume of N/10 sodium thiosulphate required for iodine trichloride left after the experiment in c.c. | Percentage amount of fat oxidised |
|-------------------|-----------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|-----------------------------------|
| 1 | Glucose | 10.8 c.c. | 15.6 c.c. | 11.5 | 37.8 |
| 2 | Urea | " | " | 11.5 | 37.8 |
| 3 | Ferrous hydroxide | " | " | 13.9 | 47.0 |
| 4 | Ferrous hydroxide and glucose | " | " | 10.5 | 22.7 |
| 5 | Ferrous hydroxide and urea | " | " | 10.5 | 22.7 |
| 6 | Ferrous hydroxide and glucose and urea | " | " | 10.0 | 15.2 |

10 c.c. of $\text{ICl}_3 + \text{KI} \equiv 17.6$ c.c. of $\text{N}/10 \text{Na}_2\text{S}_2\text{O}_3$.

10 c.c. potassium oleate + 10 c.c. $\text{ICl}_3 \equiv 10.8$ c.c. of $\text{N}/10 \text{Na}_2\text{S}_2\text{O}_3$.

10 c.c. of glucose + 10 c.c. $\text{ICl}_3 \equiv 15.6$ c.c. of $\text{N}/10 \text{Na}_2\text{S}_2\text{O}_3$.

10 c.c. of urea + 10 c.c. $\text{ICl}_3 \equiv 15.6$ c.c. of $\text{N}/10 \text{Na}_2\text{S}_2\text{O}_3$.

10 c.c. of $\text{ICl}_3 + \text{KI} \equiv 17.4$ c.c. of $\text{N}/10 \text{Na}_2\text{S}_2\text{O}_3$.

hydrates or fats, the oxidation of urea is appreciably decreased. Also in presence of urea the oxidation of fat or carbohydrate is also retarded. (Vide Tables III-V, XIV-XVI.) From our experimental results given in Table XVI, it will be seen that in presence of a mixture of fat and carbohydrate, urea is not oxidised at all. This is a very important point in understanding the metabolism in the animal body. In normal health, the heat and energy of the body are supplied to the system from the combustion of carbohydrates, fats, and proteins. Our experimental results prove conclusively that the oxidation of fats is retarded by carbohydrates and less powerfully by nitrogenous products. It seems fairly certain now that the presence of either one or two of the above substances which are undergoing oxidation, retards the oxidation of the third. In presence of an excess of fat, little protein should be burnt. It is evident that fat in the diet may avoid consumption of tissue fat and prevent too large catabolism of tissue proteins. The protein-sparing qualities of fats and carbohydrates were discovered by some of the earliest students of metabolism from feeding experiments and it is believed that carbohydrate is the most efficient of the two in sparing the proteins. It is apparent, therefore, that our experimental results as recorded in this paper

TABLE VI
Hippuric Acid

Estimation of hippuric acid in presence of (i) carbohydrates, (ii) urea, (iii) fats, (iv) freshly precipitated ferrous hydroxide, and (v) sodium sulphite, in neutral solutions. The volume of each of the solutions taken was 10 c.c. and the amount of ferrous hydroxide was 0.0674 gram and of sodium sulphite was 0.1513 gm. The volume of air passed was 36.5 litres in 5½ hours. The strength of each of the solutions of carbohydrates, urea and fats was practically 1.0%. (10 c.c. of potassium stearate \equiv 14.2 c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$; 10 c.c. of potassium oleate \equiv 10.8 c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$.)

| No. of Experiment | Substance used in the experiment as catalyst | Volume of N/10 caustic soda in c.c. required for 10 c.c. of hippuric acid taken (Blank) | Volume of N/10 caustic soda in c.c. required for hippuric acid left after the experiment | Amount of hippuric acid oxidised in terms of N/10 caustic soda in c.c. | Percentage amount of hippuric acid oxidised |
|-------------------|----------------------------------------------|-----------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|------------------------------------------------------------------------|---------------------------------------------|
| 1 | Glucose | 5.7 | 5.7 | 0.0 | Nil |
| 2 | Laevulose | " | " | " | " |
| 3 | Lactose | " | " | " | " |
| 4 | Cane sugar | " | " | " | " |
| 5 | Urea | " | " | " | " |
| 6 | Potassium stearate | " | 3.9 | 1.8 | 31.6 |
| 7 | Potassium oleate | " | 3.0 | 2.7 | 47.3 |
| 8 | Ferrous hydroxide | " | 3.8 | 1.9 | 33.3 |
| 9 | Sodium sulphite (=0.1513 gm.) | " | 2.9 | 2.8 | 49.1 |

10 cc. of hippuric acid \equiv 5.7 c.c. of N/10 NaOH.

1 c.c. of N/10 NaOH sol'n \equiv 0.0179 gm. of hippuric acid.

have adduced for the first time evidence in support of the foregoing empirical observations of the physiologists and chemists. Moreover, our results show that the oxidation of hippuric acid and glycine is considerably retarded by the presence of glucose, lactose and laevulose (Vide Tables Nos. VI and XII).

Influence of alkali:—In all our experiments, it will be seen that the amount of oxidation of fats, carbohydrates, and nitrogenous products is greater, the greater the amount of alkali. In previous papers,¹ we have emphasized that alkali is beneficial for diseases like diabetes, gout, beriberi, rickets and other types of metabolism diseases, because we have experimentally proved that carbohydrates, fats and nitrogenous products are appreciably oxidised by passing air in presence of sodium bicarbonate. There is difference of opinion among the medical men about the efficiency of alkali treatment. Thus Fürth² is definitely against alkali treatment in gout as will be seen from the following lines:—

“The constant effort to favourably influence gout by flooding the body with curative alkaline waters is without the least theoretical foundation.” On the other hand Cushny³ is in favour of alkaline treatment as will be evident

TABLE VII
Hippuric Acid

Estimation of hippuric acid in presence of (i) fat + urea, (ii) fat + glucose and (iii) fat + glucose + urea. The volume of air passed was 36.5 liters in 5½ hours.

| No. of Experiment | Substances used in the experiment as catalysts | Volume of N/10 caustic soda in c.c. required for 10 c.c. of hippuric acid taken (Blank) | Volume of N/10 caustic soda in c.c. required for hippuric acid left after the experiment | Amount of hippuric acid oxidised in terms of 10/N caustic soda in c.c. | Percentage amount of hippuric acid oxidised |
|-------------------|------------------------------------------------|-----------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|------------------------------------------------------------------------|---------------------------------------------|
| 1 | Potassium stearate and urea | 5.7 | 4.9 | 0.8 | 14.0 |
| 2 | Potassium oleate and urea | " | 4.7 | 1.0 | 17.5 |
| 3 | Potassium stearate and glucose | " | 4.8 | 0.9 | 15.8 |
| 4 | Potassium oleate and glucose | " | 4.6 | 1.1 | 19.3 |
| 5 | Potassium stearate and glucose and urea | " | 5.3 | 0.4 | 7.0 |
| 6 | Potassium oleate and glucose and urea | " | 5.1 | 0.6 | 10.5 |

10 c.c. of potassium stearate \equiv 14.2 c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$.

10 c.c. of potassium oleate \equiv 10.8 c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$.

10 c.c. of urea solution \equiv 0.1 gm. of urea.

10 c.c. of glucose solution \equiv 0.0962 gram. of glucose.

¹ J. Phys. Chem., 29, 799 (1925); 30, 277 (1926).

² "Chemistry of Metabolism", p. 184.

³ "Pharmacology and Therapeutics", 7th Edition, p. 545.

from the following quotations:— "When diabetes induces an increased acid formation in the tissues as is almost invariably the case in its later stages, the alkalis are of undoubted benefit in neutralising the oxybutyric acid formed and thus economising the alkalis of the blood. In diabetic coma, temporary improvement may be attained by the uses of large doses of alkalies." Vön Noorden was also a great advocate of alkaline treatment in diabetic coma.

From our experimental results, it will be seen that uric acid and other substances can be readily oxidised by passing air in presence of alkali at the ordinary temperature. Hence we are definitely of opinion that alkaline treatment should be efficacious in gout, diabetes, beri-beri, and other metabolism diseases, because in presence of alkali, the amount of metabolism is increased.

In previous papers,¹ we have emphasised that when glucose is not oxidised in the body, fats are likely to be oxidised rapidly not to carbon dioxide and

TABLE VIII
Urea

Estimation of urea in presence of freshly precipitated hydroxides of different metals in neutral solutions. The volume of urea used was 10 c.c. and the volumes of different salt solutions, each of 1.0% concentration, were 20 c.c. in each case. The hydroxides were precipitated from the salt solutions by the addition of the exact equivalent amount of alkali. The volume of air passed was 36.5 litres in 5½ hours.

| No. of Experiment | Substance (freshly precipitated hydroxides or sulphite) used as catalyst in the experiment | Amount of urea in gm. in 10 c.c. of the solution taken. (Blank) | Amount of urea left in gm. after the experiment | Amount of urea oxidised in gm. | Percentage amount of urea oxidised |
|-------------------|--------------------------------------------------------------------------------------------|-----------------------------------------------------------------|-------------------------------------------------|--------------------------------|------------------------------------|
| 1 | Cerous hydroxide | 0.20 | 0.17 | 0.03 | 15.0 |
| 2 | Manganous hydroxide | " | 0.1625 | 0.0375 | 18.75 |
| 3 | Ferrous hydroxide | " | 0.18 | 0.02 | 10.0 |
| 4 | Ferric hydroxide | " | 0.18 | 0.02 | 10.0 |
| 5 | Uranous hydroxide | " | 0.16 | 0.04 | 20.0 |
| 6 | Chromic hydroxide | " | 0.1725 | 0.0275 | 13.75 |
| 7 | Cobaltous hydroxide | " | 0.18 | 0.02 | 10.0 |
| 8 | Nickelous hydroxide | " | 0.18 | 0.02 | 10.0 |
| 9 | Mercuric hydroxide (wet HgO) | " | 0.1625 | 0.0375 | 18.75 |
| 10 | Cupric hydroxide | " | 0.165 | 0.035 | 17.5 |
| 11 | Lead hydroxide | " | 0.17 | 0.03 | 15.0 |
| 12 | Sodium sulphite (= 10 c.c. of 1.0% sol'n.) | " | 0.176 | 0.024 | 12.0 |

¹ J. Phys. Chem., 29, 376 (1925); "Chemie der Zelle und Gewebe," 12, 217 (1925); 13, 119 (1926).

water but to the stage of acetone bodies and that the oxidation of the glucose leads to the complete oxidation of the fats. When glucose is not burnt appreciably in the body as happens in the case of severe diabetes, the fats and proteins have to be oxidised for the supply of heat to the body and hence in diabetes, fats and proteins have to be burnt more readily than in normal health. From our experimental results, it will be seen that in the presence of carbohydrates which are undergoing oxidation, the velocity of oxidation of fats is greatly decreased. Hence in normal health and with a mixed diet, the easily oxidisable carbohydrates which have been proved to act as negative catalysts in the oxidation of fats, are necessary for the complete oxidation of fatty food materials, and the oxidation of both the substances can go on simultaneously and slowly. When the negative catalysts, the carbohydrates, are not present, the oxidation of fats proceeds rapidly and the end products

TABLE IX
Carbohydrate

Estimation of glucose, cane sugar and starch in presence of (i) 10 c.c. of caustic soda containing 0.05 gm. and (ii) 10 c.c. of urea of 2.0% solution + 10 c.c. of caustic soda containing 0.05 gm. Volume of air passed was 36.5 litres in 5½ hours.

| No. of Experiment | Substance used in the experiment | Actual amount of substance in gm. in 10 c.c. of the solution taken (Blank) | Amount of substance left in gm. after the experiment | Amount of substance oxidised in gm. | Percentage amount of substance oxidised | Remarks |
|-------------------|----------------------------------|----------------------------------------------------------------------------|------------------------------------------------------|-------------------------------------|-----------------------------------------|-----------------------------------------------------------------------------------------------------------|
| A | | | | | | |
| 1 | Glucose * | 0.0962 | 0.0853 | 0.0109 | 11.4 | Experiment performed in alkaline solution (= 10 c.c. of NaOH containing 0.05 gm.) and in absence of urea. |
| 2 | Cane sugar | 0.0964 | 0.0839 | 0.0125 | 12.9 | |
| 3 | Starch | 0.1027 | 0.0717 | 0.0310 | 30.0 | |
| B | | | | | | |
| 1 | Glucose | 0.0962 | 0.0897 | 0.0065 | 6.7 | Experiment performed in presence of urea under identical conditions as above. |
| 2 | Cane sugar | 0.0964 | 0.0935 | 0.0029 | 3.0 | |
| 3 | Starch | 0.1027 | 0.0792 | 0.0235 | 22.8 | |

*These results have been taken from our previous publication:—Palit and Dhar: J. Phys. Chem., 30, 941 (1926).

TABLE X—Urea

Estimation of urea in presence of freshly precipitated ferrous hydroxide (=0.0674 grm. of $\text{Fe}(\text{OH})_2$) and excess of alkali. The volume of air passed was 36.5 litres in 5½ hours and the volume of urea solution used was 10 c.c. of 2.0% strength.

| No. of Experiment | Volume of caustic soda added in c.c. | Amount of caustic soda added in grm. for the expt. | Amount of urea in grm. taken in 10 c.c. of the solution (Blank) | Amount of urea left in grm. after the experiment | Amount of urea oxidised in grm. | Percentage amount of urea oxidised |
|-------------------|--------------------------------------|----------------------------------------------------|-----------------------------------------------------------------|--------------------------------------------------|---------------------------------|------------------------------------|
| 1 | 0 c.c. | 0.0 | 0.20 | 0.1800 | 0.0200 | 10.0 |
| 2 | 10 c.c. | 0.05 | " | 0.1750 | 0.0250 | 12.5 |
| 3 | 20 c.c. | 0.10 | " | 0.1675 | 0.0325 | 16.2 |
| 4 | 40 c.c. | 0.20 | " | 0.1625 | 0.0375 | 18.7 |
| 5 | 60 c.c. | 0.30 | " | 0.1600 | 0.0400 | 20.0 |

TABLE XI—Glycine

Estimation of glycine in presence of (i) freshly precipitated hydroxides of different metals in neutral solutions and (ii) caustic soda, sodium bicarbonate and sodium sulphite. The volume of glycine used was 10 c.c. and the volumes of different salt solutions, each of 1.0% concentration, were 20 c.c. in each case. The hydroxides were precipitated from the salt solutions by the addition of the exact equivalent amount of caustic soda. The volume of air passed was 36.5 litres in 5½ hours.

| No. of Experiment | Substance (freshly precipitated hydroxides, caustic soda, sodium bicarbonate sulphite) used as catalyst in the experiment | Volume of N/10 caustic soda in c.c. required for 10 c.c. of glycine taken. (Blank) | Volume of N/10 caustic soda in c.c. required for glycine left after the experiment | Amount of glycine oxidised in terms of N/10 caustic soda in c.c. | Percentage amount of glycine oxidised |
|-------------------|---------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------|---------------------------------------|
| 1 | Ferrous hydroxide | 13.3 c.c. | 8.6 | 4.7 | 35.3 |
| 2 | Cerous hydroxide | " | 8.4 | 4.9 | 36.8 |
| 3 | Manganous hydroxide | " | 9.6 | 3.7 | 27.8 |
| 4 | Uranous hydroxide | " | 9.2 | 4.1 | 30.8 |
| 5 | Cobaltous hydroxide | " | 11.6 | 1.7 | 12.7 |
| 6 | Nickelous hydroxide | " | 10.2 | 3.1 | 23.3 |
| 7 | Lead hydroxide | " | 9.6 | 3.7 | 27.8 |
| 8 | Mercuric hydroxide (wet HgO) | " | 9.4 | 3.9 | 29.3 |
| 9 | Chromic hydroxide | " | 9.9 | 3.4 | 25.5 |
| 10 | Ferric hydroxide | " | 9.5 | 3.8 | 28.5 |
| 11 | Cupric hydroxide | " | 8.8 | 4.5 | 33.8 |
| 12 | Caustic soda (=100 c.c. of N/8)" | " | 9.3 | 4.0 | 30.0 |
| 13 | Sodium bicarbonate (=10 c.c. of 1.0% sol'n.) | " | 7.6 | 5.7 | 42.1 |
| 14 | Sodium sulphite (=10 c.c. of 1.0% sol'n.) | " | 3.5 | 9.8 | 73.6 |

10 c.c. of glycine \equiv 13.3 c.c. of N/10 NaOH \equiv 0.09975 grm. of glycine.

1 c.c. of N/10 NaOH \equiv 0.0075 grm. of glycine.

are not mainly carbon dioxide and water as in normal health but are β -hydroxybutyric acid, diacetic acid, acetone, etc. The rapid oxidation of fats in the absence of carbohydrates leads to the formation of acetone bodies as will be apparent from the following facts:—

(1) Ingestion of a large amount of fats without carbohydrates or proteins leads to the formation of acetone bodies.

(2) In starvation, after a few days, acetone bodies are generally found in the urine.

It is well known that by injection of insulin, acetone bodies disappear from the urine of the diabetic. This is due to the fact that by the presence of insulin, the glucose which was passing unoxidised from the diabetic system, is oxidised and the oxidation of the glucose leads to the more complete though more slow oxidation of fats.

Lusk, Landegren and others¹ proved that the withdrawal of carbohydrates from food increases the protein metabolism. Moreover, it is well known that there is a considerable tissue waste in diabetes. These facts become clear from our experimental results already recorded which prove that carbohydrates markedly retard the oxidation of nitrogenous matter.

According to J. Bär,² simple withdrawal of carbohydrates is followed in normal human beings accustomed to a mixed diet and also in apes by an acidosis, i.e. by an excretion of acetone, diacetic acid and β -oxybutyric acids along with coincident increase in the ammonia elimination.

TABLE XII
Glycine

Estimation of glycine in presence of (i) carbohydrates, (ii) urea and (iii) fats in neutral solutions. The volume of each of the solutions taken was 10 c.c. and the volume of air passed was 36.5 litres in 5½ hours. The strength of each of the solutions of carbohydrates, urea and fats was about 10% (10 c.c. of glycine \equiv 13.3 c.c. of N/10 NaOH; 10 c.c. potassium stearate + 10 c.c. ICl₃ \equiv 14.2 c.c. of N/10 Na₂S₂O₃ and 10 c.c. potassium oleate + 10 c.c. ICl₃ \equiv 10.8 c.c. of N/10 Na₂S₂O₃.)

| No. of Experiment | Substance used in the experiment as catalyst | Volume of N/10 caustic soda in c.c. required for 10 c.c. of glycine taken. (Blank) | Volume of N/10 caustic soda in c.c. required for glycine left after the experiment | Amount of glycine oxidised in terms of N/10 caustic soda in c.c. | Percentage amount of glycine oxidised |
|-------------------|----------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------|---------------------------------------|
| 1 | Glucose | 13.3 | 13.0 | 0.3 | 2.2 |
| 2 | Galactose | " | 12.7 | 0.6 | 4.4 |
| 3 | Lactose | " | 13.1 | 0.2 | 1.4 |
| 4 | Laevulose | " | 12.9 | 0.4 | 3.0 |
| 5 | Cane sugar | " | 13.25 | 0.05 | 0.3 |
| 6 | Urea | " | 12.5 | 0.8 | 6.0 |
| 7 | Potassium stearate | " | 7.3 | 6.0 | 44.3 |
| 8 | Potassium oleate | " | 8.2 | 5.1 | 37.5 |

¹ Compare Lusk: "Science of Nutrition", p. 269 (1919).

² Archiv. exp. Pathol., 54, 153 (1905).

TABLE XIII
Glycine

Estimation of glycine in presence of (i) fat + glucose (ii) fat + urea, (iii) fat + glucose + urea and (iv) excess of fats. The volume of air passed was 36.5 litres in $5\frac{1}{2}$ hours.

10 c.c. potassium stearate + 10 c.c. $\text{ICl}_3 \equiv 14.2$ c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$.

10 c.c. potassium oleate + 10 c.c. $\text{ICl}_3 \equiv 10.8$ c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$.

| No. of Experiment | Substances used in the experiment as catalyst | Volume of N/10 caustic soda in c.c. required for 10 c.c. of glycine taken. (Blank) | Volume of N/10 caustic soda in c.c. required for glycine left after the experiment | Amount of glycine oxidised in terms of N/10 caustic soda in c.c. | Percentage amount of glycine oxidised |
|-------------------|----------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------|---------------------------------------|
| 1 | Potassium stearate and glucose | 13.3 | 9.8 | 3.5 | 26.3 |
| 2 | Potassium stearate and urea | " | 10.2 | 3.1 | 23.3 |
| 3 | Potassium oleate and glucose | " | 11.1 | 2.2 | 16.5 |
| 4 | Potassium oleate and urea | " | 12.0 | 1.3 | 9.7 |
| 5 | Potassium stearate and glucose and urea | " | 11.5 | 1.8 | 13.5 |
| 6 | Potassium oleate and glucose and urea | " | 12.8 | 0.5 | 3.9 |
| 7 | Glucose and urea | " | 13.3 | 0.0 | 0.0 |
| 8 | Excess of potassium stearate (20 c.c.) and glucose | " | 6.5 | 6.8 | 51.1 |
| 9 | Excess of potassium oleate (20 c.c.) and glucose | " | 6.3 | 7.0 | 52.6 |
| 10 | Excess of potassium stearate (20 c.c.) and urea | " | 9.7 | 3.6 | 27.0 |
| 11 | Excess of potassium oleate (20 c.c.) and urea | " | 9.4 | 3.9 | 29.3 |

10 c.c. of glycine $\equiv 13.3$ c.c. of N/10 NaOH $\equiv 0.09975$ gm. of glycine.

1 c.c. of N/10 NaOH $\equiv 0.0075$ gm. glycine.

TABLE XIV
Carbohydrates

Estimation of carbohydrates in presence of fats. The volume of air passed was 60 litres in 9 hours. The volume of fat taken was 10 c.c. in each case. 10 c.c. of potassium stearate \equiv 14.2 c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$; 10 c.c. of potassium oleate \equiv 10.8 c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$.

| No. of Experiment | Substance used in the experiment | Actual amount of substance in 10 c.c. of the solution taken (Blank) | Amount of substance left in gm. after the experiment | Amount of substance oxidised in gm. | Percentage amount of substance oxidised | Remarks |
|-------------------|----------------------------------|---------------------------------------------------------------------|------------------------------------------------------|-------------------------------------|-----------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------|
| A. 1 | Arabinose | 0.1000 | 0.0974 | 0.0026 | 2.6 | Experiment performed in presence of potassium stearate (= 10 c.c.) in neutral solutions. |
| 2 | Galactose | 0.0861 | 0.0788 | 0.0073 | 8.5 | |
| 3 | Glucose | 0.0962 | 0.0906 | 0.0056 | 5.8 | |
| 4 | Laevulose | 0.09185 | 0.0904 | 0.00145 | 1.5 | |
| 5 | Lactose | 0.0997 | 0.0859 | 0.0138 | 13.8 | |
| 6 | Cane sugar | 0.0964 | 0.0896 | 0.0068 | 7.0 | |
| 7 | Maltose | 0.1097 | 0.0889 | 0.0208 | 18.9 | |
| 8 | Starch | 0.1027 | 0.0823 | 0.0204 | 19.9 | |
| B. 1 | Arabinose | 0.1000 | 0.0899 | 0.0101 | 10.1 | Experiment performed in presence of potassium stearate (= 10 c.c.) in alkaline solutions. The volume of alkali used = 10 c.c. of N/8 NaOH. |
| 2 | Galactose | 0.0861 | 0.0756 | 0.0105 | 12.2 | |
| 3 | Glucose | 0.0962 | 0.0866 | 0.0096 | 9.5 | |
| 4 | Laevulose | 0.09185 | 0.0723 | 0.0195 | 21.2 | |
| 5 | Lactose | 0.0997 | 0.0786 | 0.0211 | 21.2 | |
| 6 | Cane sugar | 0.0964 | 0.0876 | 0.0088 | 9.1 | |
| 7 | Maltose | 0.1097 | 0.0829 | 0.0268 | 24.4 | |
| 8 | Starch | 0.1027 | 0.0811 | 0.0216 | 21.0 | |
| C. 1 | Arabinose | 0.1000 | 0.0965 | 0.0035 | 3.5 | Experiment performed in presence of potassium stearate (= 10 c.c.) + ferrous hydroxide (= 0.0674 gm. of $\text{Fe}(\text{OH})_2$) in neutral solutions. |
| 2 | Galactose | 0.0861 | 0.0774 | 0.0087 | 10.0 | |
| 3 | Glucose | 0.0962 | 0.0880 | 0.0076 | 7.9 | |
| 4 | Laevulose | 0.09185 | 0.08125 | 0.0106 | 11.5 | |
| 5 | Lactose | 0.0997 | 0.0853 | 0.0144 | 14.4 | |
| 6 | Cane sugar | 0.0964 | 0.0862 | 0.0102 | 10.5 | |
| 7 | Maltose | 0.1097 | 0.0861 | 0.0236 | 21.5 | |
| 8 | Starch | 0.1027 | 0.0602 | 0.0425 | 41.3 | |

TABLE XIV (Continued)

| No. of Experiment | Substance used in the experiment | Actual amount of substance in gm. in 10 c.c. of the solution taken (Blank) | Amount of substance left in gm. after the experiment | Amount of substance oxidised in gm. | Percentage amount of substance oxidised | Remarks |
|-------------------|----------------------------------|----------------------------------------------------------------------------|------------------------------------------------------|-------------------------------------|-----------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| D. 1 | Arabinose | 0.1000 | 0.0971 | 0.0029 | 2.9 | Experiment performed in presence of potassium stearate (= 10c.c.) + ferrous hydroxide (= 0.0674 gm. of Fe (OH) ₂ + urea (= 10 c.c. of 1.0% solution) in neutral solutions. |
| 2 | Galactose | 0.0861 | 0.0820 | 0.0041 | 4.7 | |
| 3 | Glucose | 0.0962 | 0.0916 | 0.0046 | 4.8 | |
| 4 | Laevulose | 0.09185 | 0.08725 | 0.0065 | 7.1 | |
| 5 | Lactose | 0.0997 | 0.0888 | 0.0109 | 10.9 | |
| 6 | Cane sugar | 0.0964 | 0.0956 | 0.0008 | 0.8 | |
| 7 | Maltose | 0.1097 | 0.0973 | 0.0124 | 11.3 | |
| 8 | Starch | 0.1027 | 0.0642 | 0.0385 | 37.5 | |
| E. 1 | Arabinose | 0.1000 | 0.0198 | 0.0802 | 80.2 | Experiment performed in presence of potassium oleate (= 10c.c.) + ferrous hydroxide (= 0.0674 gm. of Fe (OH) ₂) in neutral solutions |
| 2 | Galactose | 0.0861 | 0.0122 | 0.0739 | 85.8 | |
| 3 | Glucose | 0.0962 | 0.0098 | 0.0864 | 89.7 | |
| 4 | Laevulose | 0.09185 | 0.01395 | 0.0779 | 84.8 | |
| 5 | Lactose | 0.0997 | 0.0813 | 0.0184 | 18.4 | |
| 6 | Cane sugar | 0.0964 | 0.0795 | 0.0169 | 17.5 | |
| 7 | Maltose | 0.1097 | 0.0617 | 0.0480 | 43.7 | |
| 8 | Starch | 0.1027 | 0.0270 | 0.0757 | 73.7 | |
| F. 1 | Arabinose | 0.1000 | 0.1000 | 0.0000 | Nil | Experiment performed in presence of potassium oleate (= 10 c.c.) + ferrous hydroxide (= 0.0674 gm. of Fe (OH) ₂) + urea (= 10c.c. of 1.0% solution) in neutral solutions. |
| 2 | Galactose | 0.0861 | 0.0861 | 0.0000 | Nil | |
| 3 | Glucose | 0.0962 | 0.0962 | 0.0000 | Nil | |
| 4 | Laevulose | 0.09185 | 0.0918 | 0.0000 | Nil | |
| 5 | Lactose | 0.0997 | 0.0977 | 0.0020 | 2.0 | |
| 6 | Cane sugar | 0.0964 | 0.0963 | 0.0001 | Nil | |
| 7 | Maltose | 0.1097 | 0.1020 | 0.0077 | 7.0 | |
| 8 | Starch | 0.1027 | 0.0784 | 0.0243 | 23.7 | |

TABLE XV
Glucose

Estimation of glucose in presence of potassium oleate and freshly precipitated hydroxides of different metals. The volume of potassium oleate used was 10 c.c. and the volumes of different salt solutions used were 20 c.c. in each case. The hydroxides were precipitated from the salt solutions by the addition of the exact equivalent amount of caustic soda. The volume of air passed was 60 litres in 9 hours. (10 c.c. of Pot. oleate \equiv 10.8 c.c. of N/10 $\text{Na}_2\text{S}_2\text{O}_3$).

| No. of Experiment | Substance (freshly ppted. hydroxides) used in the experiment as catalyst | Amount of glucose in gm. in 10 c.c. of the solution taken (Blank) | Amount of glucose left in gm. after the experiment | Amount of glucose oxidised in gm. | Percentage amount of glucose oxidised | Remarks |
|-------------------|--------------------------------------------------------------------------|-------------------------------------------------------------------|----------------------------------------------------|-----------------------------------|---------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1 | Cerous hydroxide | 0.0962 | 0.0764 | 0.0198 | 20.6 | Experiment performed in presence of freshly precipitated hydroxides of different metals, potassium oleate and glucose in neutral solutions. The strength of salt solutions used was 1.0% in each case. |
| 2 | Cobaltous hydroxide | " | 0.0519 | 0.0443 | 46.0 | |
| 3 | Ferrous hydroxide | " | 0.0098 | 0.0864 | 89.7 | |
| 4 | Ferric hydroxide | " | 0.0344 | 0.0618 | 64.2 | |
| 5 | Manganous hydroxide | " | 0.0604 | 0.0358 | 37.2 | |
| 6 | Mercuric hydroxide (wet HgO) | " | 0.0362 | 0.0600 | 62.4 | |
| 7 | Nickelous hydroxide | " | 0.0461 | 0.0501 | 52.0 | |
| 8 | Uranous hydroxide | " | 0.0503 | 0.0459 | 47.7 | |

TABLE XVI

Urea

Estimation of urea in presence of mixtures of freshly precipitated ferrous hydroxide (= 0.0674 gm.) and carbohydrates and potassium oleate in neutral solutions. The volume of air passed was 60 litres in 9 hours. The volume of each solution taken was 10 c.c. in each case. (10 c.c. of potassium oleate + 10 c.c. of $\text{ICl}_3 \equiv 10.8$ c.c. of $\text{N}/10 \text{Na}_2\text{S}_2\text{O}_3$.)

| No. of Experiment | Substance used as catalyst in the experiment | Amount of urea in gm. in 10 c.c. of the solution taken. (Blank) | Amount of urea left in gm. after the experiment | Amount of urea oxidised in gm. | Percentage amount of urea oxidised |
|-------------------|----------------------------------------------|-----------------------------------------------------------------|-------------------------------------------------|--------------------------------|------------------------------------|
| 1 | Arabinose | 0.20 | 0.19 | 0.01 | 5.0 |
| 2 | Galactose | " | 0.19 | 0.01 | " |
| 3 | Glucose | " | 0.19 | 0.01 | " |
| 4 | Laevulose | " | 0.20 | 0.0 | Nil |
| 5 | Lactose | " | " | " | " |
| 6 | Cane sugar | " | " | " | " |
| 7 | Maltose | " | " | " | " |
| 8 | Starch | " | " | " | " |

Strength of carbohydrate solutions was about 1.0%.

It is generally believed by physiologists that carbohydrates are oxidised in the animal economy most readily but our experimental results show that fats are also readily oxidised.

In a previous paper,¹ we have explained that glycosuria induced by the intake of phosphorus, arsenic, or phlorhizin or ether, is really due to the decrease in the velocity of oxidation of carbohydrates by the presence of the above reducing agents. As soon as the oxidation of carbohydrates is decreased by the presence of reducing agents like phosphorus, arsenic, phlorhizin or ether, etc., glycosuria sets in and when glucose escapes unburnt from the system, the retardation of the oxidation of the fats and proteins due to the oxidation of glucose cannot take place and thus we get acidosis in all these cases.

In the same paper, it was shown that small quantities of alcohol might be useful in decreasing acidosis in diabetes, because alcohol being a substance which is readily oxidised can retard the oxidation of fats and thus may lead to the more complete but slow oxidation of fats. Xylose, gluconic acid, propionic acid, citric acid, glutaminic acid, glutaric acid, etc., have been found to decrease acidosis and formation of acetone bodies in diabetes. We are of opinion that the action of these substances is similar to that of alcohol as they are all reducing agents and are likely to reduce the velocity of the oxidation of fats and hence are likely to act as anti-ketogenic substances by checking the formation of acetone bodies.

¹ "Chemie der Zelle und Gewebe", 13, 119 (1926).

We are trying to obtain quantitative and comparative results on the velocity of oxidation of fats, proteins, and carbohydrates by air and thus establish definitely whether fats or carbohydrates are oxidised more readily in the system.

Summary and Conclusions

(1) Experimental results show that nitrogenous substances like urea, hippuric acid, and glycine can be oxidised by air at the ordinary temperature in presence of reducing agents. In presence of alkali, hippuric acid and glycine can be oxidised even in the absence of a catalyst and the greater the amount of alkali, the greater is the amount of oxidation.

(2) Experimental results have been obtained showing that in presence of caustic soda or sodium bicarbonate, potassium stearate and potassium oleate have been oxidised. The amount of oxidation is increased in presence of different metallic hydroxides.

(3) From a mixture of carbohydrates, and potassium stearate or potassium oleate, both the carbohydrates and fats are oxidised by passing air at the ordinary temperature and in presence of caustic alkali or sodium bicarbonate, the amount of oxidation is increased and the greater the amount of alkali, the greater is the amount of oxidation. In presence of ferrous hydroxide or cerous hydroxide, the amount of oxidation of fats and carbohydrates is increased from a mixture.

(4) The experimental results conclusively prove that the amount of oxidation of carbohydrates is greatly decreased by the presence of fats. Also the oxidation of fats is reduced by the presence of carbohydrates. Moreover, in presence of carbohydrates or fats the oxidation of urea, hippuric acid and glycine is appreciably decreased. In presence of urea, the oxidation of fat or carbohydrate is also retarded.

(5) These experimental results have thrown considerable light on the metabolism in the animal body in normal health and in diabetes.

(6) We are of opinion that alkaline treatment should prove efficacious in gout, diabetes, beri-beri, rickets and other metabolism diseases, because in presence of even sodium bicarbonate, the amount of oxidation of fats, carbohydrates, and nitrogenous substances is greatly increased.

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June, 1937.*

THE STRUCTURE OF WATER

BY S. W. PENNYCUICK

In recent years attention has been recalled to the problem of valence and co-ordination numbers, and it is generally accepted that (with very few exceptions) each element can exercise, and does exercise, valence forces in excess of that fixed number which had for so many years been assigned to it. The oxygen atom possesses (and exercises) a very active auxiliary valence and forms numerous molecular compounds, sometimes referred to as oxonium compounds, in which the oxygen atom can show a maximum co-ordination number of 4. The evidence in favour of a strong residual oxygen field is now quite extensive.¹ Further, hydrogen has a co-ordination number 2,² and therefore in many of its compounds it can still exert an attraction on the lone electron pairs of other elements. The evidence for the existence of these molecular compounds is also very extensive.³ The simplest compound of these two elements is H-O-H, and this paper concerns itself largely with the simple explanation of various phenomena that follow from the assumption that the auxiliary valence fields of both hydrogen and oxygen in the water molecule are not only very active, but also have a strong attraction for one another.

The Structure of the Water Molecule

The numerous unique properties of water,—the high dielectric constant, the solvent activity, the remarkable and general catalytic activity, and even the physiological importance—must finally be traced to the structure of the individual molecule itself, and an examination shows that this structure is in most respects unique. In the first place the molecule is polar and is therefore unsymmetrical, and as there now seems to be little doubt that the saturated oxygen atom possesses tetrahedral structure⁴, the water molecule is most satisfactorily represented by the tetrahedron in Fig. 1, where the electrons are in pairs at tetrahedron corners.⁵ (The oxygen nucleus with its two helium

¹ See chiefly Nagnet: *Compt. rend.*, 58, 381, 675 (1860); Friedel: *Bull.*, (2) 24, 166, 241 (1875); Hantzsch: *Z. physik. Chem.*, 61, 157 (1907); 65, 41 (1908); Homfray: *J. Chem. Soc.*, 87, 1443 (1905); Irvine and Moodie: *J. Chem. Soc.*, 89, 1578 (1906); Falk and Nelson: *J. Am. Chem. Soc.*, 37, 1732 (1915); Kendall and Booge: 38, 1712 (1916); Tschelinzeff: *Bull.*, (4) 35, 741 (1924); 37, 181 (1925); Morgan and Smith: *J. Chem. Soc.*, 125, 1997 (1924); Picard: *Helv. Chim. Acta*, 7, 800 (1924); Sidgwick and Callow: *J. Chem. Soc.*, 125, 527 (1924); 127, 908 (1925).

² Sidgwick: *J. Chem. Soc.*, 123, 726 (1922); *Trans. Faraday Soc.*, 19, 11, 469 (1923).

³ See chiefly Lowry: *J. Soc. Chem. Ind.*, 42, 43 (1923); Lowry and Burgess: *J. Chem. Soc.*, 123, 2111 (1923); Lowry and Cutter: 125, 1466 (1924); Morgan and Smith: *J. Chem. Soc.*, 125, 1997; Sidgwick and co-workers: 527 (1924); G. N. Lewis: "Valence"; Werner: "New Ideas in Inorganic Chemistry".

⁴ Picard: *Helv. Chim. Acta*, 7, 800 (1924); Main Smith: "Chemistry and Atomic Structure".

⁵ Huggins: *Phys. Rev.*, (2) 27, 281 (1926).

electrons is omitted). The simplicity of the total electronic structure in this molecule must be emphasised, for like the CH_4 molecule it possesses only the two closed shells of neon with a total of 10 electrons. This simplicity of structure, in conjunction with the foregoing, allows us to assume that all the auxiliary valence effects are due directly to the two lone oxygen pairs or to the bivalence of the hydrogen nuclei, the two helium electrons in the inner shell having a very minimum of disturbing action. The polarity of the molecule is obvious from the structure above, and hence water can attach itself

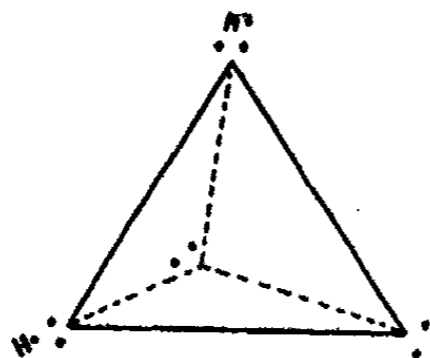


Fig. 1

to other molecules, as experiment indicates, either through its own *negative* pairs, or through its own *positive* hydrogen nuclei, which accounts for the "positive and negative" affinity of the water molecule as outlined by Briggs.¹ Further, the molecular volume of the water molecule is relatively small (according to Fraenkel², the diameter is 1.7×10^{-8} cm.), and as there are four active points of auxiliary attack, it is not surprising that the molecule

shows such great activity. Numerous simple indications, such as the great difficulty experienced in removing the last traces of water from a substance, and the remarkable catalytic properties of traces of water vapour, point to the fact that the atoms in the H-O-H molecule are in especially favourable positions to use their auxiliary fields. The characteristic peculiarities of the structure outlined above will be shown to be quite sufficient to account for various of the unique properties of this compound.

The Structure of Ice

The X-ray analysis of ice supports Bragg's view³ that each oxygen atom is surrounded by four atoms of hydrogen, and that each hydrogen atom lies symmetrically between two atoms of oxygen. Thus in the ice crystal each oxygen atom is exerting its maximum co-valence of four, and each hydrogen atom its maximum of two, or, what is the same thing, each water molecule is completely utilising its four auxiliary bonds. It is significant (from the point of view of the tetrahedral water molecule) that the crystal structure of ice is directly comparable with that of the diamond. In fact the former can be obtained from the latter by replacing each carbon by an oxygen atom, inserting a hydrogen nucleus between each pair of oxygen atoms, and making a very simple parallel planar shift (Figs. 2A and 2B). Just as the carbon atoms in diamond may be said to form hexagonal, six carbon rings, so the oxygen atoms in ice form hexagonal six oxygen rings, but with an alternating hydrogen nucleus. Ice thus forms a network in three dimensions of H-O-H rings, each containing six H-O-H molecules. It is quite probable (Bragg) that in such a structure the primary bonds are of the same strength as the secondary and that therefore the whole is symmetrical. It is important to stress the sim-

¹ J. Chem. Soc., 93, 1564 (1908); 115, 278 (1919).

² J. Russ. Phys. Chem. Soc., 49, 87 50, 5, (1918).

³ Proc. Phys. Soc. London, 34, 98 (1922).

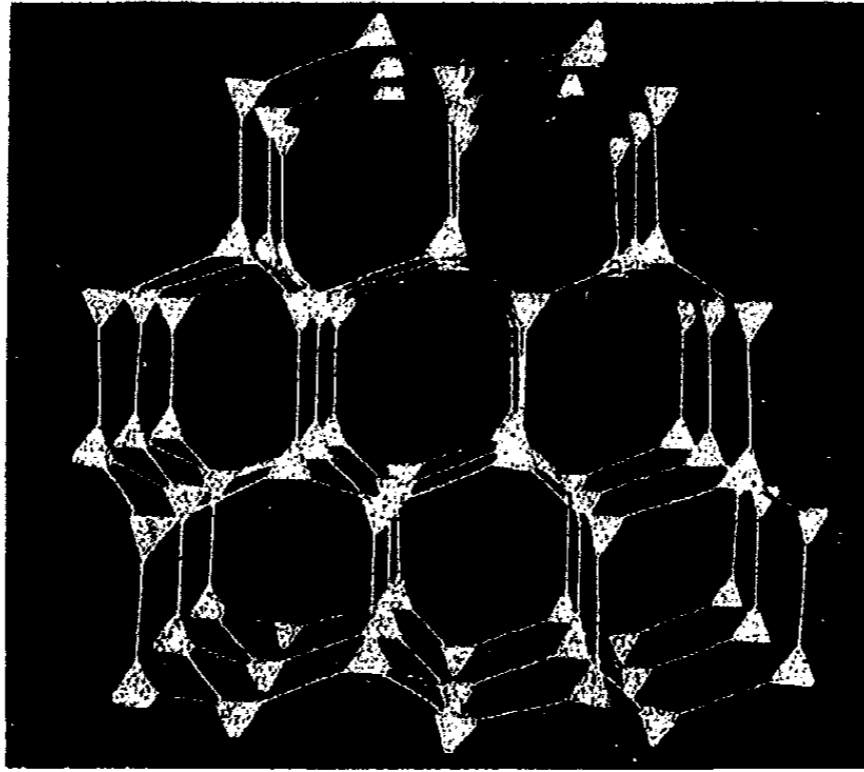


FIG. 2A

Fig. 2A is a photograph of a model of the diamond crystal, showing each carbon atom as a tetrahedron with a valence of four. The figure shows the 6 carbon (benzene) ring formation. The top layer of atoms is identical with and superposable on, the bottom layer, i.e. the structure repeats itself every fourth layer.

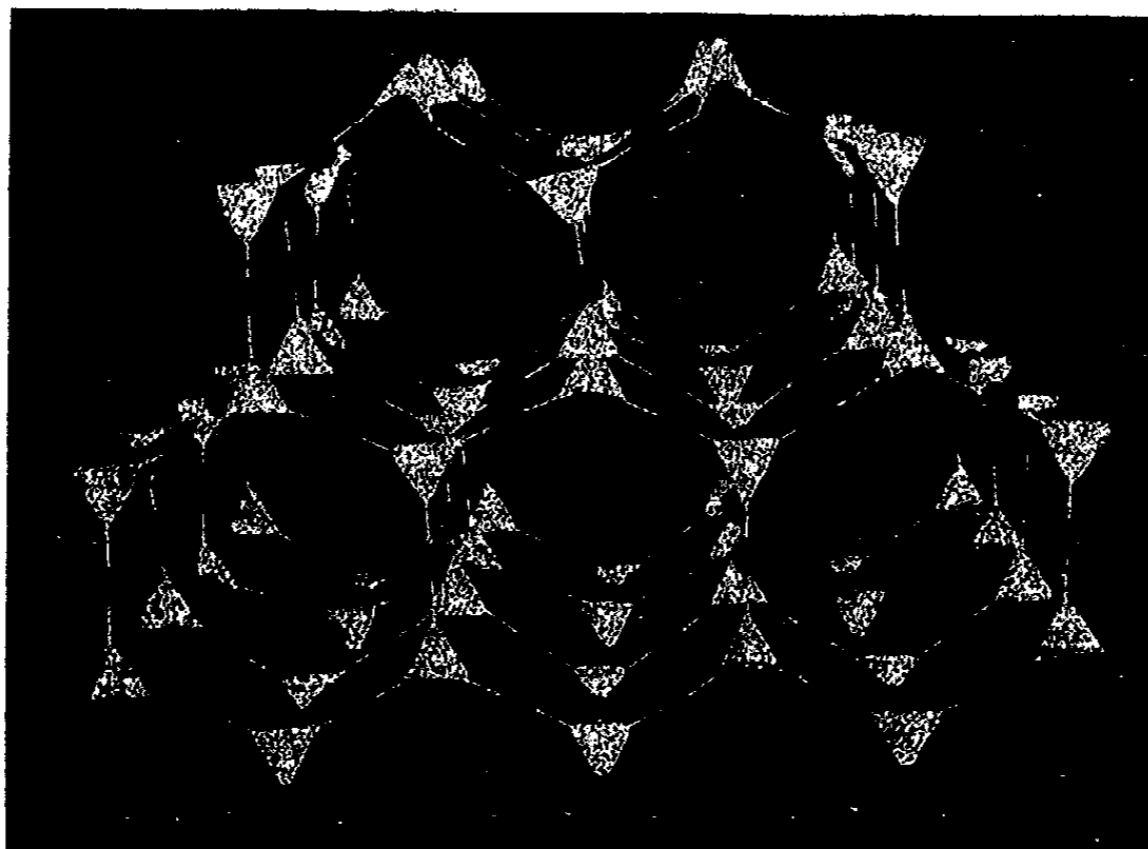


FIG. 2B

Fig. 2B is a photograph of a model of the ice crystal (after Bragg). The tetrahedra represent the oxygen atoms with a saturated co-valence of 4, and the interlying dark balls represent the hydrogen atoms (or nuclei) with a saturated co-valence of 2. The structure is even more regular than that of the diamond, and the boat-shaped (benzene) rings, here containing 6 oxygen atoms, stand out. The top layer of atoms is identical with, and superposable on, the bottom layer, and the structure repeats itself every third layer.

licity of this structure, and to emphasise again that the *only* bonds between the molecules appear to be the active auxiliary bonds with which H-O-H forms its numerous co-valent compounds. If these be the only bonds between the molecules in the solid state, then we can have no reason for assuming that the *liquid* molecules are held by other than the same co-valent bonds. (For, speaking generally, we should expect that known auxiliary bonds play an important part in liquid structure, but that in the case of solids owing to the decreased molecular energy, quite new bonds due to outer electronic rearrange-

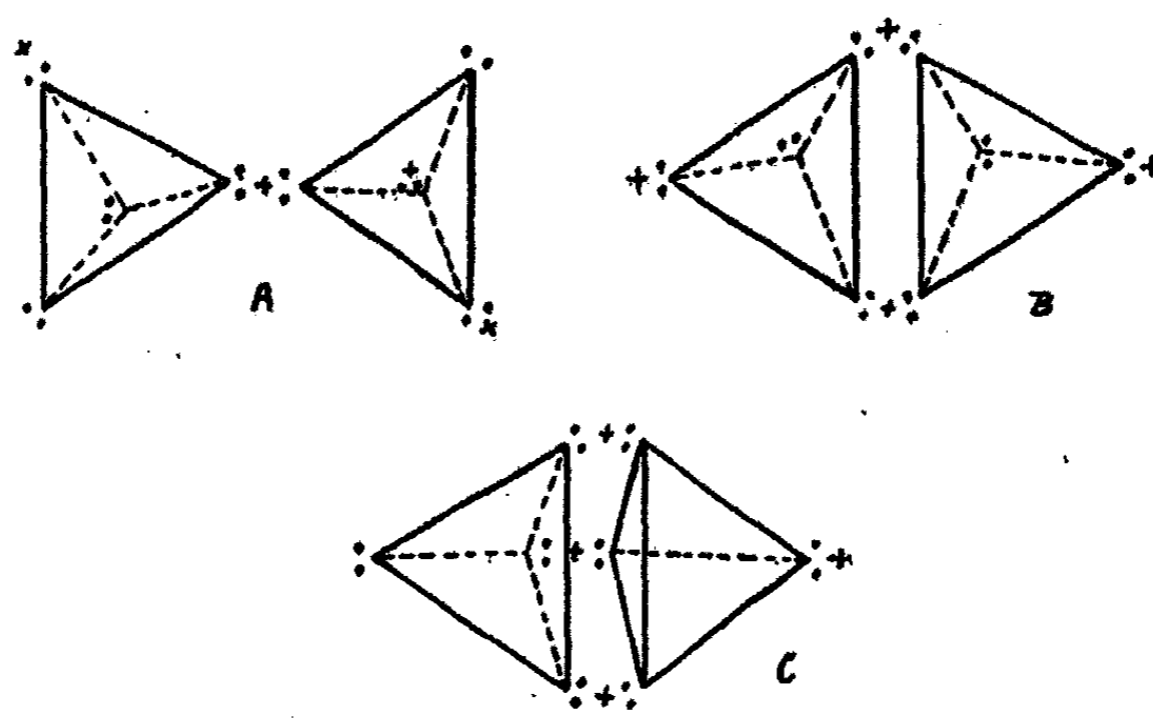


FIG. 3

ments might come into action. In the structure of ice there is no evidence of such new bonds, and hence there is no need to presuppose such in water structure). It has been suggested¹ that the association of molecules in liquid H-O-H is due to the particular secondary bonds under discussion. But in view of the foregoing is there any necessity to imagine the existence of any other form of bond between the water molecules *in general*? It is attempted in this paper to show that the various properties of water can be explained on the assumption that the molecules are held together solely through the attractions between the hydrogen nuclei and the oxygen lone electron pairs.

The Condensation of H-O-H Molecules

When a gaseous H-O-H molecule at condensation temperature enters the auxiliary field of a second, then assuming the tetrahedral structure, combination can take place at the apices of the tetrahedra concerned. The (H-O-H)₂ molecule so formed could exist as one of the structures shown in Fig. 3. The structures B and C require an approach of the oxygen nuclei, and general chemical evidence shows such to be rare even in the case of strong primary fields. It is therefore probable that structure A more accurately represents the facts (Picard). Owing to the simple and symmetrical structure of the molecule (two hydrogen nuclei and two lone pairs), the types of double mole-

¹ Latimer and Rodebush: J. Am. Chem. Soc., 42, 1431 (1920).

cules A are strictly limited, for whenever one molecule unites with a second the mode of union is always of the same form, namely the linking of a hydrogen nucleus with an oxygen lone pair. This union is accompanied by some energy manifestation due to a change in the electronic orbits at the junction and probably at other points in the molecule, the total effect being the latent heat.

Now, when one polar molecule combines with a second the compound molecule is more polar still, as is evident from Fig. 4. Or, more particularly, when one water molecule attracts and holds the hydrogen nucleus of a second,

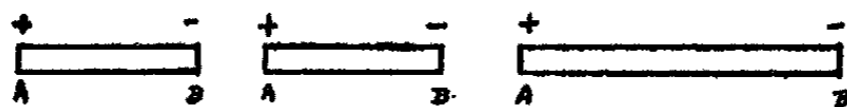
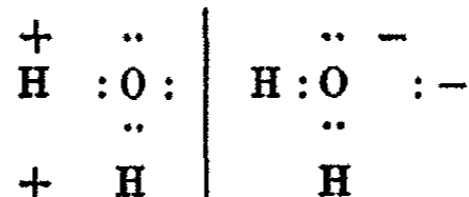
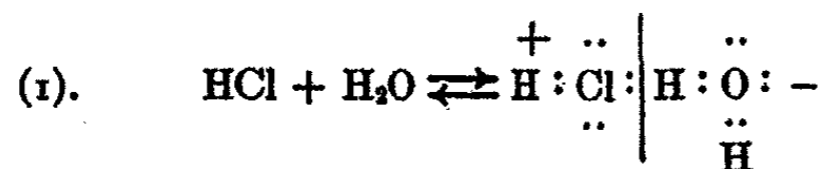


FIG. 4

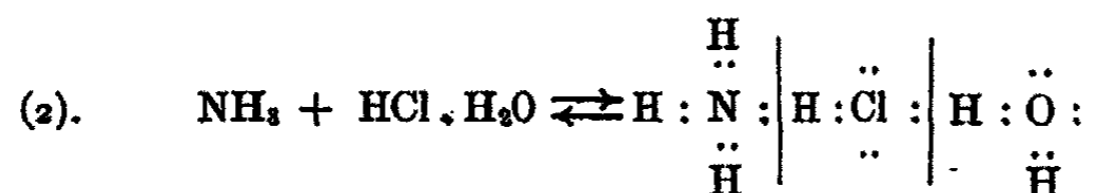
its attraction on its own hydrogen nuclei is lessened. We can thus represent the polar $(\text{H-O-H})_2$ molecule, in two dimensional notation, as



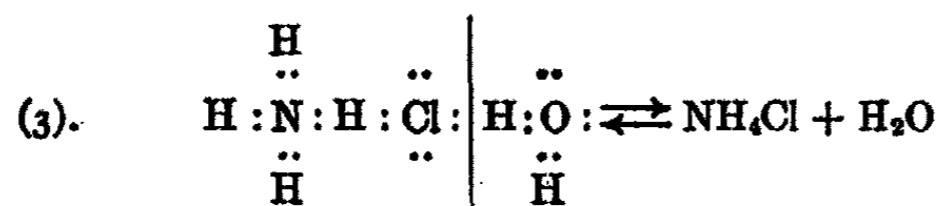
This molecule has two active hydrogen nuclei and two active oxygen lone pairs, and in this respect strangely resembles the single water molecule. (The third hydrogen nucleus and the third electron pair are probably less active. Such a molecular activation on combination through auxiliary bonds, seems to be quite a general phenomenon. For example water vapour acts catalytically by "opening up" the residual fields of one or both of two stable molecules. In the case of $\text{NH}_3 + \text{HCl}$, the action may follow these lines,



The HCl molecule is now more polar and sufficiently active to attach itself to the NH_3 lone pairs, as in



and finally,

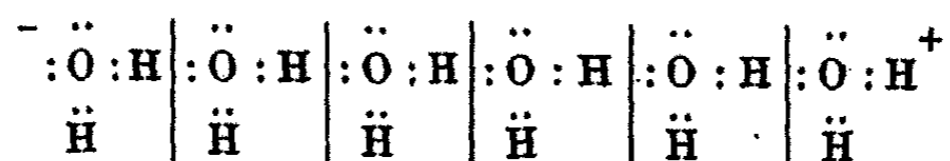


Or again, when a gaseous H-O-H molecule is captured through its auxiliary field by some foreign surface, its exposed field is now more active than the normal, and further as it has surrendered some of its kinetic energy, it now

acts as an efficient condensing agent towards other water molecules; hence the condensation of water vapour on nuclei. It may also be concluded that the strong attraction which exists between water and almost all substances, causing water to be classed¹ as "a special contamination" which is completely removable only with very great difficulty, is due primarily to the water itself, for in addition to the fact that the latter has such strong auxiliary fields, these active fields are both "positive" and "negative" and can thus neutralise practically any foreign field.

The Structure of Water

When a third molecule of water approaches an H-O-H pair it adds on through a hydrogen nucleus or a lone electron pair in the foregoing way. Hence we get (H-O-H)₃ and then (H-O-H)₄ and so on. These tend to form polar chains as below



Although the end molecules of the chain are the most active, the interlying molecules are not wholly inactive, and the lesser tendency towards the formation of side chains plays an important part in determining the mobility of the liquid. (In the solid state the growth of the side chains is of fundamental importance and gives the system a definite structure). So far as we know, the individual molecules in the liquid state possesses translational, vibrational, and a certain amount of rotational energy. The total molecular energy, limits the length of the polar chains and continually breaks the longer ones at the weaker links. But there is another factor influencing the size of these chains. The two dimensional regularity in the above figure is diagrammatic only, the actual chains will be irregular and distorted because of tetrahedral structure, and if the ends of a chain combine or neutralise one another the resulting closed chain or ring will be relatively inactive. Various considerations lead us to believe that such closed chains play a very important part in the structure of water.

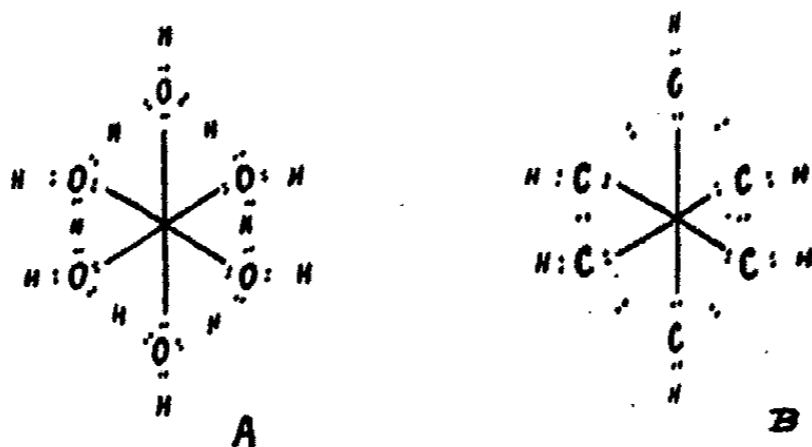
The hexagonal structure of the ice crystal together with the tetrahedral structure of the water molecule, point definitely to the conclusion that if such stable rings are formed in water, they must contain six oxygen nuclei and be represented by Fig. 5A. Such an (H-O-H)₆ ring bears a striking resemblance to the inactive benzene ring, particularly when it is kept in mind that the alternating hydrogen in the former ring is quite inactive (co-valence 2), and probably occupies a small volume.

Now the general evidence points undoubtedly to the association of the water molecule, and, in *Trans. Faraday Soc.*, 6, 71 (1910), it is concluded after some exhaustive discussion, that water consists of some (H-O-H)₃ ("ice") molecules, a large percentage of (H-O-H)₂ molecules, and some single molecules; and some such idea is generally accepted at the present day. The

¹ Smits: "Theory of Allotropy" (1922).

structure of ice shows however, that the term ice molecule has no meaning, but that if there any unit of compound molecular structure in the ice crystal that unit is not the $(\text{H-O-H})_2$ molecule but the $(\text{H-O-H})_6$.

It must be here stressed that while various methods depending on variations in the surface tension, in the boiling-point, in the latent heat, in the viscosity, in the cohesion, and in other physical properties, all agree that water (among other liquids) is abnormal and that the abnormality can always be explained by some form of association; the value of the degree of association is quite another matter. In fact all of the known methods give association values which are open to serious question. Their merits and demerits have



FIGS. 5A and 5B

often been discussed, and are reviewed by Tyrer¹. Tyrer concludes that none of the usual methods is sufficiently theoretically sound to give a reliable value for the association factor. He also shows that a new boiling-point equation which he develops gives the association factor of water throughout its bulk (not at the surface only) as having a minimum value of six. It would be well at this stage to ask the question, "What do we really understand by liquid association?" A little consideration shows that the idea is far from self evident. For instance all liquids must be associated in a general sense by virtue of their being liquids, for in all liquids there must be attractions between the molecules and hence a statistical association. Smits submits very definite evidence that complexity in the liquid state is a "perfectly general" phenomenon, and the evidence indicates that even in the so-called normal liquids, such as benzene, there is an inner equilibrium between different aggregates of molecules. Further, Duclaux² maintains that the equation of state can be deduced equally well by substituting the idea of molecular association, for van der Waals' conception of internal pressure.

Now in the crystal the atom is the only real unit of structure, and each atom under the attractions of its neighbours possesses zero resultant field. In the liquid state however, the molecule preserves its individuality, although the intermolecular forces may, and do, act through particular atoms. Owing primarily to the greater molecular energy and the consequent greater mobility, liquid systems lack definite structure and the resultant field on any particular

¹ Phil. Mag., (6) 20, 522 (1910); Z. physik. Chem., 50, 80 (1912); J. Phys. Chem., 19, 81 (1915).

² J. Phys. Radium, (6) 6, 199 (1925).

molecule is not zero. We must conclude then that in any liquid, each molecule is at any instant more strongly attached to some one particular neighbour and less strongly to other neighbouring molecules; and that the whole system forms a three-dimensional continually-changing and branching network in which the linkings are of varying strength, and in which it is difficult to imagine the existence of a single or completely uncombined molecule even as a rare occurrence. Every normal liquid must possess this kind of association, but it is questionable whether the term "degree of association" can have any real quantitative meaning in these cases. Van der Waals¹ considers that the molecules in normal liquids tend to form loosely combined groups which for an instant behave as single molecules. He calls this quasi-association, and further expresses the belief² that no equation of state is possible unless one postulates an association of molecules to larger complexes. Further, Garver³ finds that the normal liquids are all associated; whilst Tyrer suggests that the quasi-associated molecules in any liquid may have a mean kinetic energy less than that of the external (gas) molecules, and suggests this as a real distinction between quasi- and true association.

Accepting as we must, that normal liquids show a loose structure and through this a quasi-association, due inherently to intermolecular attractions, where then lies the difference in structure of the abnormal or so-called associated liquids? The abnormalities displayed by the latter as revealed by the various methods already mentioned, and the fact that these abnormalities always indicate a larger molecular weight than normal (although perhaps of uncertain or variable value), point undoubtedly to the conclusion that there is a real difference between their structure and that of normal liquids. Yet we have no reason for believing that such real association, in the case of water at all events, would be due to other than the usual auxiliary fields.

The author suggests that real association does take place through auxiliary fields, but has a quantitative meaning, only when two or more united polar molecules present an abnormally weakened field to the surroundings and thus have independent existence within relatively wide time limits. The difference between associated and normal (quasi-associated) liquids then lies in this,—though both show molecular combinations through auxiliary fields, the compound molecule in an associated liquid presents an abnormally weakened field to the surroundings, while the compound molecule (if the term may still be used) in a normal liquid possesses a strong field by means of which it tends to grow and to become immediately incorporated into the whole liquid system. As it is quite impossible to obtain any idea of the degree of this quasi-association, the latter liquids are referred to as normal.

In the case of associated liquids we might well imagine several molecules combining so as to neutralise their active fields by forming a ring, as in Fig. 6. Such a compound would behave as a solute molecule, moving through the solution as an independent unit, until such time as it was opened up and thus

¹ Proc. K. Akad. Wet. Amsterdam, 13, Pt. I, 107 (1910).

² "Die Zustandsgleichung" (1911).

³ J. Phys. Chem., 16, 454, 669 (1912).

incorporated into the solvent. Water being polar and abnormal must polymerise in the above manner and from what has already been said the polymerised unit seems to be $(\text{H-O-H})_6$. It is important to notice that the polymerisation is due only to the relatively stable rings which are formed, and that as soon as the rings are broken polymerisation disappears and the system becomes normal and quasi-associated. We cannot accept the view that water is a mixture of mono-, di- and tri-hydrol each having a statistical average existence, because such a system would behave as a normal quasi-associated liquid; rather must we consider water as a mixture of relatively stable compound molecules of benzene ring structure in a normal (quasi-associated) solvent.

We might even regard water as an initial attempt of the H-O-H system to build up its hexagonal crystal structure; and whilst the auxiliary fields of the molecules are strong enough to build as far as the single $(\text{H-O-H})_6$ ring, the molecular energies are sufficiently great to destroy any further crystal growth. The relative inactivity of such rings would ensure their existence as individuals, and play an important part (together with the molecular energy) in limiting further growth.

The fraction of water so polymerised is uncertain, and at all events would vary with the temperature; and as we are not dealing with a single liquid but rather with an unusual solution in which solute $(\text{H-O-H})_6$ and solvent (H-O-H) are interconvertible and in equilibrium, it is questionable whether we can draw any simple deductions from the usual abnormality factors. Perhaps the researches of Richards and co-workers on the compressibility of water¹ may be taken as giving the most probable values of the percentage association. They conclude that at 20° water contains about 28% of polyhydrol.

Other Associated Liquids

Although this paper concerns itself with the liquid system water only, and is so restricted because of the interpretation put on the local auxiliary fields of the H-O-H molecule, still it is of interest to examine some related associated liquids in terms of the generalisation "association must be due to a number of liquid molecules so arranging themselves as to present a much weakened field to the surroundings."

After water, the alcohols and the organic acids are the most consistently abnormal liquids. The simpler alcohols, possessing the structure R-O-H, will show somewhat similar auxiliary fields to those of water, modified by the presence of the alkyl radical R-. Of the auxiliary fields of the latter we know little, except that the hydrogen atoms of the alkyls, being non-polar, appear

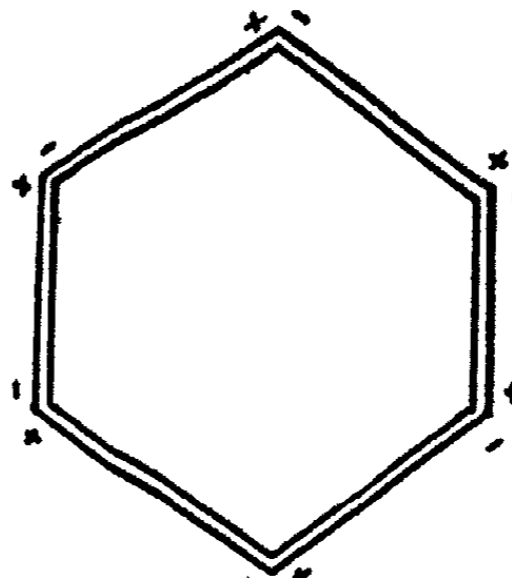


FIG. 6

¹ J. Am. Chem. Soc., 47, 2283 (1925) and previous papers.

to be less active and thus exhibit smaller tendencies to satisfy their maximum co-ordination 2. As the hydroxyl ends of the molecules are the more active, these liquids distinctly resemble water and form very similar co-ordination compounds. We should expect association to take place through these the strongest of the auxiliary fields, and hence by analogy with water we should expect, first, polar compounds as in Fig. 7A, and finally inactive ring compound molecules after the manner of Fig. 7B.

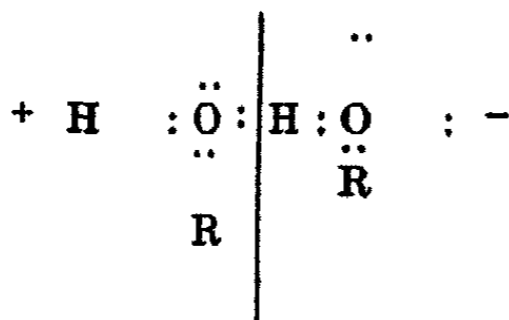


FIG. 7A

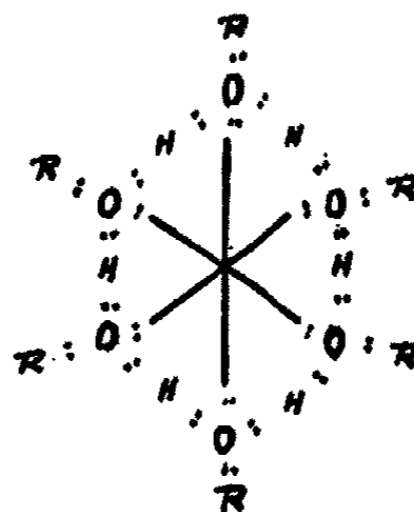


FIG. 7B

As the general investigations on crystal structure have not as yet given any insight into the bonds between the molecules nor the relative atomic positions in solid alcohol, the above structure can only be regarded as a suggestive type of alcoholic association.

Some of the organic acids however are especially interesting, for although the various quantitative methods for association show serious disagreement for most liquids, they agree remarkably well in pointing to the bimolecular state of various organic acids, particularly acetic (Tyrrer). This agreement is probably due to the fact that whilst the other associated liquids are equilibrium mixtures of associated and non-associated molecules, i.e. are really solutions, acetic acid in particular exists almost wholly as $(\text{RCOOH})_2$. These acids also show very marked association in the gaseous state, acetic acid again showing practically twice its normal molecular weight. When we add to the above, the evidence put forward by Innes¹ and by Brown and Bury² that organic acids in hydrocarbon and other normal solvents, show, at higher concentrations, abnormally large molecular weights which reach a maximum of twice the normal and never exceed this, then we must conclude that the bimolecular condition is an exceedingly favourable state for the organic acid molecule. Now, Bragg³ shows that in the solid state organic acids are always united with their COOH ends in pairs; and there is in fact every evidence that the active fields of organic acid molecules are associated with these polar COOH groups. So that if we assign the strong auxiliary effects to the oxygen lone electron pairs and hydrogen nuclei of these groups, and imagine two

¹ J. Chem. Soc., 81, 682 (1902).

² J. Phys. Chem., 30, 694 (1926).

³ Chemistry and Industry, 1926, 245.

molecules to combine as in Fig. 8 (Lewis) we obtain a compound molecule which satisfies the necessary criteria for true association. It is of interest that we have the six kernel ring again, this time with two hydrogen nuclei. Owing to the organic acids exhibiting association even in the gaseous state, we must conclude that their auxiliary fields are exceedingly active, and the above rings very stable, and hence it is not surprising that in the liquid state acetic acid should show evidence of total polymerisation to form the molecule $(RCOOH)_2$.

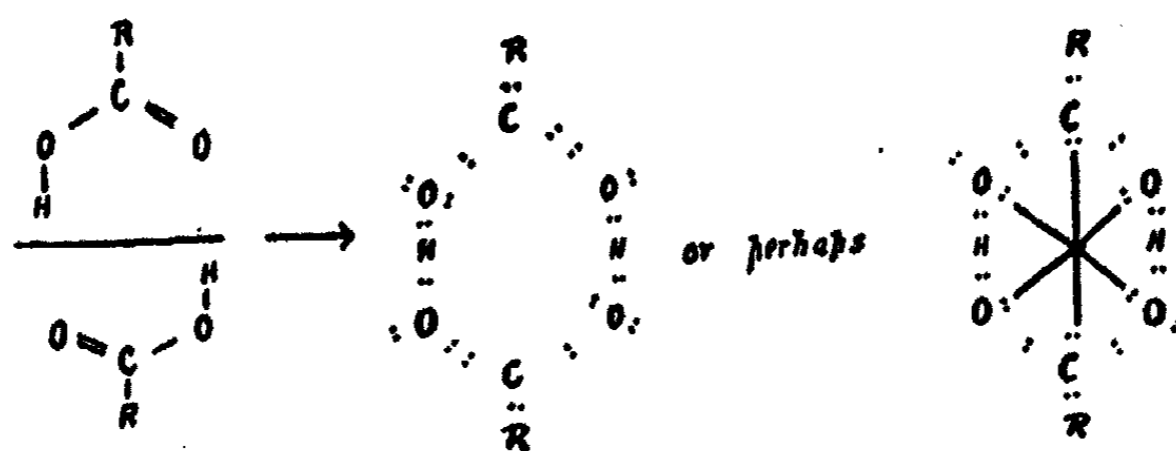


FIG. 8

Some of the Properties of Water

The various properties of aqueous systems may now be considered in terms of the above form of association, and as is seen below the evidence is strikingly in favour both of ring association and of the activity of the oxygen lone electron pairs and the hydrogen nuclei of the water molecule.

The Effect of Pressure on the System

An increase in pressure decreases the abnormality, i.e. the association, and at very high pressure, 2500 atmospheres, the liquid behaves as normal¹. If association were due to the formation of more or less stable chains in the system, it would be reasonable to expect that pressure would increase and not decrease the association. If however, as is here suggested, molecular association is due to the relatively stable rings outlined above, and only to these rings, then, as the latter cause the structure to be more open, the effect of a pressure increase is to compress and break these rings and thus cause the association to disappear. In the same way an increase of pressure on ice partially breaks the crystal ring structure and the ice melts.

The Maximum Density of Water

The existence of a maximum density at 4° may be connected with the above form of association in the following way. As Bragg has pointed out, the crystal structure of ice is extremely empty and it is very easy to imagine a less rigid arrangement of water molecules occupying less space. When ice melts at 0°, some of the associated rings still persist; this causes the structure to be more open and therefore the density to be less than if there were no such association. This is in agreement with the work of McLeod² who shows that

¹ Bridgman: Proc. Am. Acad., 47, 538 (1912).

² Trans. Faraday Soc., 21, 145 (1925).

association (in the case of water) results in a gain in volume "owing to the bulky nature of the associated molecule." As the temperature is raised the stability of these rings, and hence the association, decreases, and thus the system tends to contract or to become more dense. On the other hand there is the opposing effect, namely the increase of molecular energy with temperature and the consequent wider spacing of the attracting centres. It is very probable that the minimum shown at 4° on the temperature-volume curve is due to the alternate predominance of these opposing effects, and that from 0° to 4° the contraction due to the breaking of the associated rings is greater than the expansion due to the usual kinetic separation. Above 4° the latter change predominates.

The Latent Heat

Although the crystal bonds are necessarily of great strength the energy required to melt one gram of ice is not abnormally great. This is evidently due to the fact that the process of fusion is not a breaking of all the intermolecular bonds; in fact few bonds may be actually broken, many may be loosened and some quite unaffected. On the other hand the process of vapourisation necessitates the breaking of all the intermolecular bonds, and as some of these have persisted from the solid state the very great latent heat of steam is not surprising. The value of the fraction of the latent heat that can be ascribed to the dissociation of the complex molecules at the boiling point is invariably very high, and is believed to be about 3/5 of the total latent heat (Tyrer).

The Effect of a Solute

Speaking generally it may be said that a solute is held in solution because it possesses auxiliary fields which the solvent is able to neutralise; and the extreme solvent power of water is thus due to the exceptional activity of the spare fields of the water molecule. Hydration and solvation not only accompany but are actually the fundamental cause of solution. Now when a substance is introduced into water, it will be attacked by the more active, i.e. the unassociated molecules, and thus there will be a change in the water equilibrium and a decrease in the number of associated molecules. The decrease in the degree of association on the addition of a solute, can account satisfactorily for the corresponding lowering of the temperature of the maximum density of water, and the decrease in compressibility.¹

Water of Crystallization

The fact that the most numerous of the salts that contain water of crystallisation, (about 40% of the total), are those that contain 6, 7 or 12 molecules of water has often been commented upon. Werner has incorporated these hydrates into his general co-ordination theory, and writes them



Rhodes², however, points out the inadequacy of this theory as applied to these

¹ See Drucker: *Z. physik. Chem.*, 52, 641 (1905).

² *Chem. News*, 122, 85 (1921).

compounds, and suggests formulae of the following type, where the six water molecules exist as a unit, Fig. 9. Such six H-O-H rings with all the auxiliary linkings through the oxygen atoms were first suggested by Kohlrausch.

In view of the foregoing it is very probable that six H-O-H rings (with the auxiliary linkings as in Fig. 5A) exist as units in the crystal. Crystals with twelve molecules of water contain two such rings, while crystals with seven molecules of water contain one such ring and have one odd water molecule, the latter assumption being based on the fact that hepta-hydrated salts have one molecule of water differentiated from the other six, e.g. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ on heating loses $6\text{H}_2\text{O}$ at 100° , and the seventh water molecule at red heat.

The Self-ionisation of Water

In the ice crystal it appears that all the inter-atomic bonds are of equal strength (Bragg), and that therefore each hydrogen nucleus is equidistant from its two adjacent oxygens. Accordingly when the ice system is melted, the hexagonal associated $(\text{H-O-H})_6$ molecules, which are carried unbroken into the liquid system, are still held together as units by equivalent forces, or in other words the primary and the auxiliary bonds in the ring compound molecule (Fig. 10) are indistinguishable. Such a compound molecule could then

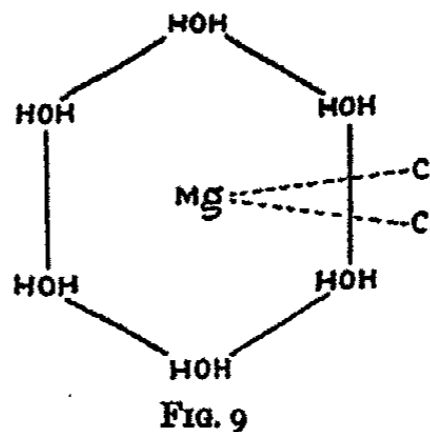


FIG. 9

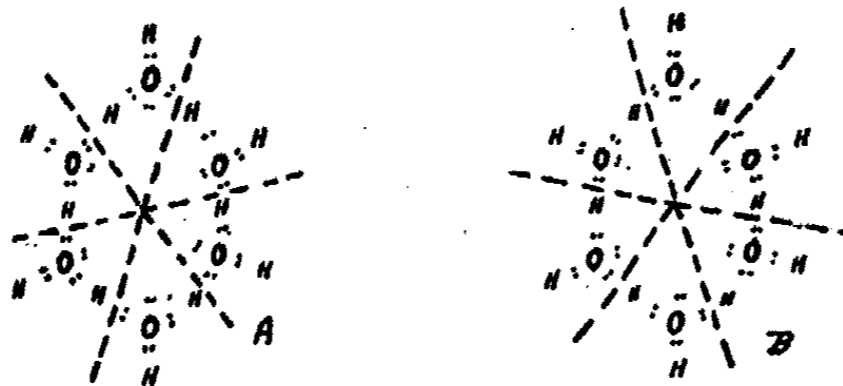


FIG. 10

break (under equal chance) either as in A or as in B, Fig. 10, to give in each case exactly the same products, namely six molecules of water. There is however this interesting difference, six water molecules could unite as shown by the dotted lines in A above and then would stand an equal chance of breaking as in B, in which case each water molecule will have interchanged an hydrogen nucleus with a neighbouring molecule, or in other words, each hydrogen nucleus in the ring will have changed its auxiliary bond into a normal primary, and its primary into an auxiliary. Owing to the symmetrical structure of the above compounds, such an interchange could not of itself give rise to any abnormal or unique effects in the system. The greater part of water, however, does not consist of these associated and relatively stable rings, but of irregular polar chains (rings in the making), represented approximately as in Fig. 11.

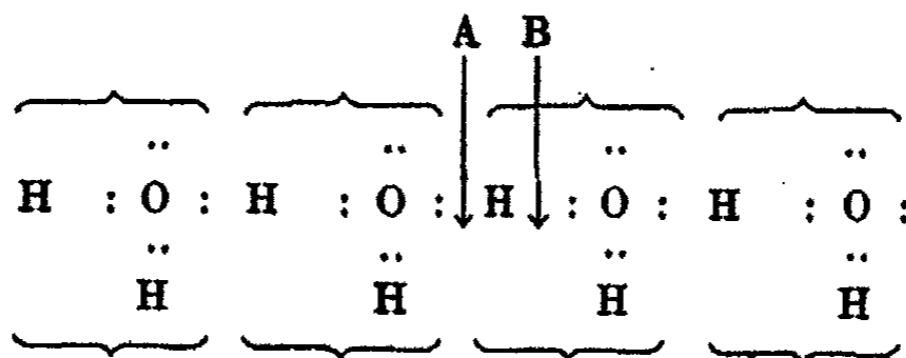


FIG. 11

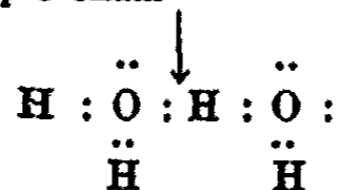
The relative strengths of the primary and auxiliary bonds in these chains is of course quite unknown, but it may be assumed (keeping the associated molecules in mind) that as the chain grows, the primary bonds grow weaker and the auxiliary stronger. In such a continually changing system, it may so happen, when conditions are especially favourable, that the polar chain instead of breaking at its normal breaking point A, breaks at B, the hydrogen nucleus concerned becoming attached to quite a different water molecule. The conditions would then be represented, momentarily and very incompletely by



Such a rupture would account for the self-ionisation of water. It is evidently of very rare occurrence, for the ionisation constant of water indicates that at ordinary temperatures only one hydrogen nucleus out of every 1,000,000,000 is so transferred at any instant.

The Di-electric Constant

Although the rupture of polar chains to produce the (hydrated) hydrogen and hydroxyl ions is very rare, the normal rupture of such chains must be of remarkably frequent occurrence. When such a normal rupture occurs, e.g. at the arrow head in the simple chain

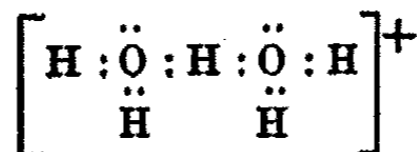


the binding hydrogen must be displaced for a very short time from its normal position in its own particular water molecule. Such a continually occurring displacement accounts for the high d.e.k. of water.

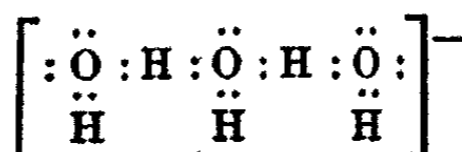
It is of interest to notice that of the other common liquids which show high di-electric constants, the chief are the simpler alcohols and the simpler fatty acids. These all possess lone oxygen electron pairs and ionisable hydrogen nuclei, and as has been shown probably combine through such in the liquid state. Their high di-electric constants are then probably due to a similar cause to that outlined above, namely to a short-time displacement of a hydrogen nucleus under the influence of the field due to an oxygen lone electron pair.

The Abnormal Velocities of Hydrogen and Hydroxyl Ions

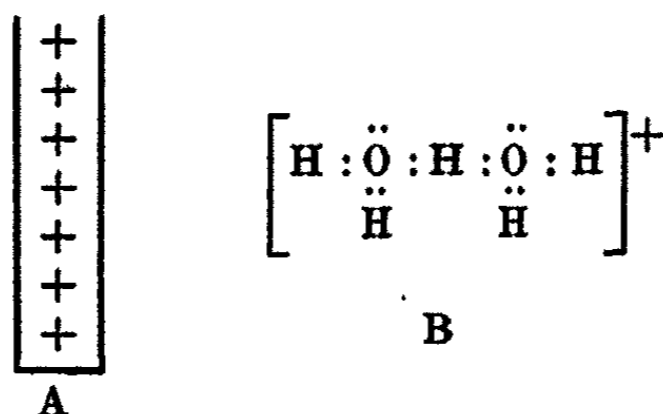
In virtue of the foregoing it is evident that the ions of water, cannot be dissociated from the contiguous water molecules which brought them into existence, or in other words these ions are always hydrated. In the same way the hydrogen ions of acid solutions are always directly associated with the surrounding water molecules. A hydrogen ion would then be more correctly written in some such form as



and an hydroxyl ion as



where the ionic groups are continually increasing or decreasing the amount of water with which they are associated. Now, in these hydrated ions it is impossible to say which of the (removable) hydrogen nuclei (four above), may be taken as representing the hydrogen ion, or which of the removable hydroxyl radicals (two above) may be the hydroxyl ion, rather must we assume the whole hydrate to carry the positive or negative charge. Under the stress of a difference of potential these ionic groups migrate towards the two poles with probably normal ionic velocities; but the difference of potential may have (in the case of these two particular ions) an added abnormal effect. For if A represent



the positive pole of an applied E.M.F. and B a hydrated hydrogen ion, then of the four removable hydrogen nuclei, those furthest from A will be the more readily removed or the more active; and during the normal continual hydration and dehydration, water will be added on at this active end and given up at the end nearest to A. This is equivalent to an abnormal increase in the velocity of the hydrogen ion. A similar explanation holds with the hydroxyl ion.

It will be noticed that whilst other ions, such as Na^+ and Ca^{++} (undoubtedly hydrated), have an individual existence in aqueous systems, the hydrogen and hydroxyl ions in such systems do not exist as unchanging individuals, but, owing to the nature of the solvent, the particular nucleus which may be arbitrarily taken as representing a hydrogen ion at any one

instant, may exist at another as part of a water molecule, the liberated hydrogen nucleus becoming the hydrogen ion. Perhaps we have here the most common example of tautomeric hydrogen.

The catalytic effect of the hydrogen ion on hydrolyses in general, is probably intimately connected with this tautomeric change; for a water molecule undergoing such a change would be in a peculiarly unstable (loosened) condition, and as such would be particularly open to internal rupture¹.

Summary²

The wide, general evidence of the activity of the auxiliary fields of the hydrogen and oxygen atoms in the water molecule, and its bearing on the idea of the association of such molecules is discussed.

The difference between quasi- and true association is pointed out, and it is concluded, in conformity with the X-ray structure of ice, that the associated molecule in liquid water is the $(\text{H}_2\text{O})_6$ molecule, and that water is a mixture of relatively stable compound molecules of benzene ring structure in a normal (quasi-associated) solvent.

The ring structure of associated acetic acid molecules is shown to be in conformity with this view.

The evidence derived from the effect of pressure on aqueous systems, the addition of a solute, the maximum density of water, the latent heat, the dielectric constant, the self-ionization, and the abnormal velocities of the hydrogen and hydroxyl ions, is shown to be strikingly in favour of ring association and of the abnormal activity of the auxiliary fields of the oxygen and hydrogen atoms.

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¹ See Pennycuick: *J. Am. Chem. Soc.*, 48, 6 (1926).

² My attention has recently been called to a paper by Simons and Hildebrand: *J. Am. Chem. Soc.*, 2183, (1924) where it has been shown from vapour density measurements, that hydrogen fluoride vapour consists of an equilibrium mixture of HF and $(\text{HF})_6$. In conjunction with the foregoing, this is very significant, particularly when one considers the close similarity in electronic structure between the hydrogen fluoride molecule and the water molecule.

THE SYSTEM: AMMONIUM SULPHATE—SULPHURIC ACID—ETHYL ALCOHOL

BY H. B. DUNNICLIFF, A. L. AGGARWAL AND R. C. HOON

Introduction

Dry ethyl alcohol rapidly extracts about two thirds of the sulphuric acid from pure dry ammonium hydrogen sulphate and a partial esterification follows¹. When ammonium sulphate is treated with alcoholic sulphuric acids of various concentrations, interaction takes place until equilibrium between the liquid phase and the solid phase is established. As in the case of the system; sodium sulphate—sulphuric acid—ethyl alcohol² the system: ammonium sulphate—sulphuric acid—ethyl alcohol is best studied by the action of alcohol or alcoholic sulphuric acids on ammonium hydrogen sulphate. If the normal salt and alcoholic sulphuric acids are used, an acid sulphate is formed on the outside of the particles of ammonium sulphate and it is very difficult to obtain quantitative results or true equilibrium owing to the protection of the inner portions of the ammonium sulphate by the acid sulphates formed. The method using the acid salt (NH_4HSO_4) and alcohol is available only until the ratio of the quantity of ammonium hydrogen sulphate to that of alcohol is so great that the resulting "Rest" and liquid phase are inseparable. For higher concentrations of the acid, alcoholic sulphuric acids and ammonium hydrogen sulphate are used and sufficient time is given for equilibrium to be established.

Experimental

Pure, dry ethyl alcohol (B.P. 78° at 742.5 mm; sp. gr. 0.7950 at 22°C = 99.9%) pure dry ammonium hydrogen sulphate (H_2SO_4 = 42.53%, NH_4 = 15.60%. Theory for NH_4HSO_4 requires H_2SO_4 = 42.61%, NH_4 = 15.67%) and 100% sulphuric acid and the alcoholic sulphuric acids were prepared by standard methods³.

Weighed quantities of ammonium hydrogen sulphate and alcohol or alcoholic sulphuric acids were sealed off in glass bulbs of about 10 c.c. capacity and shaken for about 48 hours in the former case and 8 to 15 days in the latter, in a thermostat maintained at $18.1 \pm 0.05^\circ\text{C}$ by electrical control. The tube was then allowed to remain stationary in the bath until the solid phase had settled to the bottom. The liquid was separated and analysed as described below and the residue ("Rest") was examined separately, the same method being used for both liquid phase and "Rest". Since the partial esterification of the sulphuric acid is a complicating factor in the problem, it is necessary to determine:—

¹ Dunicliff: *J. Chem. Soc.*, 121, 476 (1923).

² Dunicliff, Sikka and Hoon: *J. Phys. Chem.*, 30, 1211 (1926).

³ Butler and Dunicliff: *J. Chem. Soc.*, 117, 651 (1920).

(a) the acidity due to free sulphuric acid together with that due to ethyl hydrogen sulphate. The latter was calculated as sulphuric acid and is called the "direct acidity",

(b) the amount of sulphuric acid converted into ethyl-hydrogen-sulphate calculated as sulphuric acid is called the "combined acidity",

(c) the ammonium sulphate and

(d) the remainder of the constituents (water + alcohol + ethyl hydrogen sulphate) by difference. This is called the "solvent".

Methods of Determination

1. A weighed amount of the liquid phase or the "Rest" was titrated against standard caustic soda solution using methyl orange as indicator and the acidity calculated as parts of sulphuric acid per 100 parts of the substance. This is the "direct acidity".

2. The ammonium sulphate in each case was determined by boiling the weighed phase with excess of caustic soda, passing the ammonia evolved into standard sulphuric acid and subsequent back titration against standard caustic soda.

3. The combined acidity was estimated by titrating each of the weighed phases against standard caustic soda solution, then boiling with excess of standard caustic soda solution, evaporating to dryness and heating the residue to 120°C in an electric oven. The excess of the caustic soda solution added is partly used to decompose the ammonium salts giving ammonia and sodium sulphate and partly in hydrolysing the ester. The excess remains as free alkali and is estimated by titration against the standard sulphuric acid solution. The caustic soda used for the decomposition of the ester is determined by subtracting the amount of caustic soda used for boiling off ammonia plus that which remained as free alkali, from the total amount of caustic soda added after determining the "direct acidity". This acidity is recorded in the tables as "H₂SO₄ as ester".

Many estimations were made and of these a number are given in Tables I and II. It was desired to find the best method of representing these results graphically and it was thought that, making certain limitations, this might be done by the usual method for a condensed ternary system. Owing to the complication introduced by the esterification of the acid, it was necessary to consider which would be the best of three possible ways of condensing the system to one of three components.

I. (a) Ammonium sulphate, (b) sulphuric acid assuming that no esterification had taken place, (c) alcohol.

II. (a) Ammonium sulphate, (b) "direct acidity" (V.S.) (c) "solvent" i.e. 100 - (a+b).

III. (a) Ammonium sulphate, (b) sulphuric acid existing as such and omitting acidity due to the ethyl hydrogen sulphate, i.e. "free H₂SO₄" as recorded in the tables, (c) "Solvent", i.e. alcohol + ethyl hydrogen sulphate + water.

TABLE I
Action of Alcohol on Ammonium Hydrogen Sulphate

| In Liquid Phase | | Liquid Phase | | In Rest | | "Rest" | | Calculated acidity of solid phase % | | |
|--------------------------|---------------------------------------|---------------------------------------------------|-----------|-----------------|-------------------------------------------|--------------------------------------------------------|-----------|-------------------------------------|-------|-------|
| Total acidity as ester % | H ₂ SO ₄ Free % | (NH ₄) ₂ SO ₄ % | Solvent % | Total acidity % | H ₂ SO ₄ as ester % | Free (NH ₄) ₂ SO ₄ % | Solvent % | | | |
| 3.28 | 0.28 | 2.72 | 0.35 | 96.93 | 13.71 | 0.50 | 12.71 | 45.00 | 42.29 | 20.43 |
| 3.61 | 0.38 | 2.85 | 0.65 | 96.50 | 13.47 | 0.45 | 12.57 | 45.38 | 42.05 | 20.07 |
| 4.29 | 0.42 | 3.45 | 0.80 | 95.75 | 13.94 | 0.47 | 13.00 | 47.49 | 39.51 | 19.71 |
| 5.02 | 1.02 | 2.98 | 0.62 | 96.40 | 12.23 | 0.98 | 10.27 | 36.95 | 52.78 | 19.09 |
| 4.51 | 0.35 | 3.81 | 0.62 | 95.57 | 15.30 | 0.44 | 14.42 | 53.71 | 31.87 | 19.73 |
| 5.52 | 0.15 | 5.22 | 0.72 | 94.06 | 14.50 | 0.19 | 14.12 | 51.72 | 34.16 | 19.19 |
| 7.02 | 0.21 | 6.62 | 0.66 | 92.72 | 15.00 | 0.44 | 14.12 | 46.85 | 39.03 | 19.57 |
| 7.39 | 0.21 | 6.97 | 0.66 | 92.37 | 14.93 | 0.22 | 14.49 | 46.81 | 38.70 | 19.92 |
| 9.20 | 1.01 | 7.18 | 0.69 | 92.13 | 14.18 | 0.63 | 12.92 | 40.93 | 46.15 | 19.08 |
| 11.90 | 1.38 | 9.14 | 0.68 | 90.18 | 16.39 | 1.00 | 14.39 | 42.73 | 43.24 | 19.23 |
| 16.53 | *2.53 | 11.47 | 0.56 | 87.97 | 24.18 | 1.99 | 20.20 | 40.55 | 39.25 | 27.39 |

3(NH₄)₂SO₄, H₂SO₄
requires 19.84% H₂SO₄

2(NH₄)₂SO₄, H₂SO₄
requires 27.10% H₂SO₄

*In the last sample equal weights of alcohol and ammonium hydrogen sulphate were used. An attempt was made to ascertain the "true solid phase" when the ratio of salt to alcohol was 1.8 : 1. The mixture could not be separated into liquid phase and "Rest", so the reaction mixture was extracted with dry ether in a Soxhlet to remove alcohol, water, ester and free sulphuric acid. The solid phase so obtained had an acidity of 26.76% corresponding with the formula 2(NH₄)₂SO₄, H₂SO₄. (Theory requires H₂SO₄ - 27.10%).

TABLE II
Action of Alcoholic Sulphuric Acids on Ammonium Hydrogen Sulphate

| Acidity of alcoholic sulphuric acid before action. Approx. % | In Liquid Phase | | Liquid Phase | | In Rest | | "Rest" | | Calculated acidity in true solid phase % | | | |
|--------------------------------------------------------------|-------------------------------------------------|------------------------------------------------|-------------------------------------------------|----------------------------------------------------------------|-------------------------------------------------|----------------------------------------------------------------|-------------------------------------------------|----------------------------------------------------------------|------------------------------------------|-------|-------|----------------------------------------------------------------------------------------------------------------------------------------|
| | Total H ₂ SO ₄ as ester % | Free H ₂ SO ₄ as ester % | Total H ₂ SO ₄ as ester % | Free (NH ₄) ₂ SO ₄ Solvent % | Total H ₂ SO ₄ as ester % | Free (NH ₄) ₂ SO ₄ Solvent % | Total H ₂ SO ₄ as ester % | Free (NH ₄) ₂ SO ₄ Solvent % | | | | |
| 10 | 17.23 | 2.23 | 12.77 | 0.99 | 86.24 | 18.71 | 0.75 | 17.21 | 50.72 | 32.07 | 19.84 | 3(NH ₄) ₂ SO ₄ , H ₂ SO ₄ requires 19.84% H ₂ SO ₄ |
| 15 | 18.13 | 3.08 | 11.97 | 1.04 | 86.99 | 26.64 | 0.89 | 24.86 | 45.13 | 30.01 | 31.65 | 3(NH ₄) ₂ SO ₄ , |
| 20 | 22.22 | 4.37 | 13.48 | 1.15 | 85.37 | 29.17 | 0.99 | 27.19 | 46.82 | 25.99 | 33.15 | 2H ₂ SO ₄ requires |
| 25 | 24.45 | 5.48 | 13.49 | 1.28 | 85.23 | 37.98 | 2.25 | 33.48 | 38.90 | 27.62 | 43.06 | 33.11% H ₂ SO ₄ |
| 30 | 28.35 | 6.13 | 16.09 | 1.70 | 82.21 | 38.75 | 2.88 | 32.99 | 30.59 | 36.42 | 46.43 | |
| 35 | 31.10 | 6.92 | 17.26 | 2.03 | 80.71 | 39.02 | 2.12 | 34.78 | 40.02 | 25.20 | 42.73 | |
| 40 | 39.99 | 10.74 | 18.51 | 1.19 | 80.30 | 39.87 | 3.34 | 33.19 | 33.65 | 33.16 | 43.52 | |
| 45 | 42.19 | 10.89 | 20.41 | 1.20 | 78.39 | 41.84 | 3.81 | 34.22 | 33.32 | 32.46 | 43.98 | |
| 50 | 47.83 | 10.98 | 25.87 | 1.50 | 72.63 | 44.33 | 3.92 | 36.49 | 33.12 | 31.39 | 43.80 | (NH ₄) ₂ SO ₄ , |
| 55 | 51.36 | 11.01 | 29.34 | 1.83 | 58.83 | 46.27 | 3.95 | 38.37 | 35.02 | 26.61 | 42.33 | H ₂ SO ₄ requires |
| 60 | 56.61 | 11.23 | 34.15 | 1.95 | 63.90 | 47.93 | 3.96 | 40.01 | 36.45 | 23.54 | 43.43 | 42.61% H ₂ SO ₄ |
| 65 | 58.43 | 11.65 | 35.13 | 2.05 | 62.82 | 49.09 | 3.99 | 41.11 | 37.01 | 21.88 | 44.29 | |
| 70 | 63.41 | 12.05 | 39.31 | 2.56 | 58.13 | 51.11 | 4.01 | 43.09 | 37.94 | 18.97 | 44.92 | |
| 75 | 66.63 | 12.06 | 42.51 | 5.94 | 51.55 | 51.33 | 4.25 | 42.83 | 33.40 | 23.77 | 43.12 | |

80% and upwards.

No solid phase
No crystals separated at -18°C

When the results were plotted on the usual (condensed system) triangular isothermal diagram, the first method was shown to be inadmissible. It is not feasible to ignore esterification though the values at low concentrations of sulphuric acid are small.

Method 2 gave a rough convergence of the conjugation lines but a much more satisfactory convergency of the lines to foci on the ammonium sulphate—sulphuric acid line was given when the results were plotted according to method 3. These are shown in Fig. 1 and indicate the existence of solid phases having the formulae as shown in the diagram. The "compound"

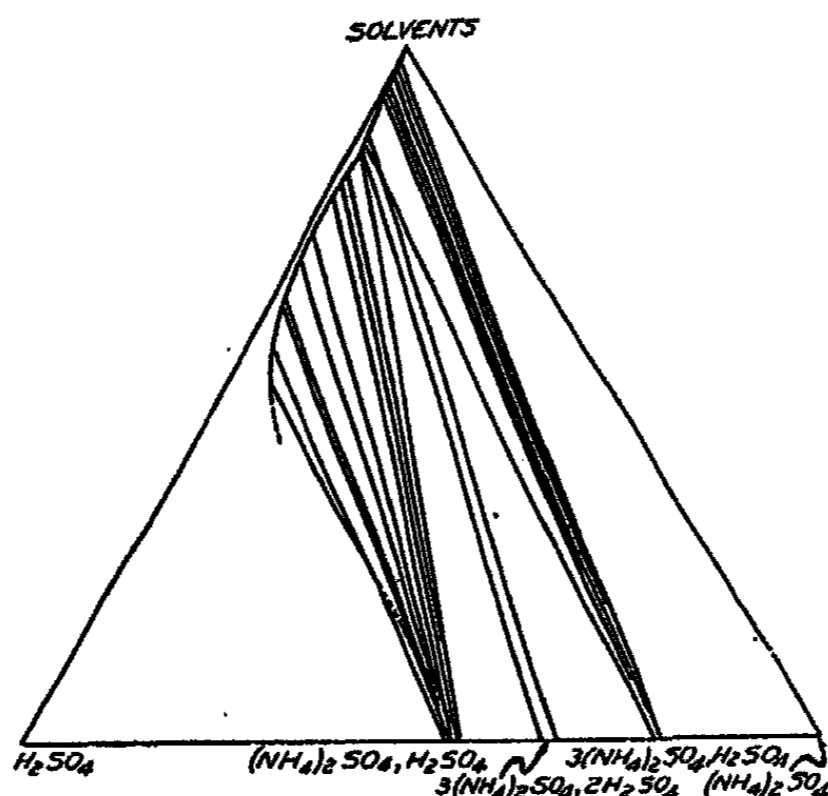


FIG. 1

$3(\text{NH}_4)_2\text{SO}_4, 2\text{H}_2\text{SO}_4$ is probably a solid solution or a mixture. The results indicate that, at low concentration of the acid, the ester has only a small influence on the equilibrium. The effect of the ester on the equilibrium when it is present in large proportions is dealt with later.

These results obtained graphically were checked by calculation. The liquid phase is homogeneous and may therefore be analysed for its constituents direct. The true solid phase exists in the "Rest" which is heterogeneous and comprises at least two phases intimately mixed:

1. true liquid phase of known composition;
2. true solid phase.

It was shown by draining a series of samples of "Rests" on porous tiles in desiccators containing phosphoric anhydride that the true solid phase contained no ester in combination. The maximum amount of ester observed in the residue was 0.12%. Since the ethyl hydrogen sulphate is peculiar to the liquid phase and knowing its percentage in the liquid phase and in the "Rest", it is possible to calculate the amount of the true liquid phase associated with the true solid phase to constitute the "Rest" and hence, by difference, the

composition of the true solid phase. Adopting this principle there are two possible ways of calculating the composition of the true solid phase:—

- (a) from the amount of ester in the "Rest" and
- (b) from the amount of solvent in the "Rest".

Since the quantity of ester in the "Rest" is small, method (b) gives the more reliable results and the calculation is carried out as follows:—

$$\begin{aligned} \text{Free H}_2\text{SO}_4 \text{ present in the Rest} \\ \text{due to liquid phase (L.P.)} &= \frac{\text{Solvent in Rest}}{\text{Solvent in L.P.}} \times \text{Free H}_2\text{SO}_4 \text{ in L.P.} \\ &= F \end{aligned}$$

$$\begin{aligned} \text{Free H}_2\text{SO}_4 \text{ present in the true} \\ \text{solid phase} &= \text{Free H}_2\text{SO}_4 \text{ in Rest} - F \\ &= F_s \end{aligned}$$

$$\begin{aligned} \text{(NH}_4\text{)}_2\text{SO}_4 \text{ present in Rest due} \\ \text{to L.P.} &= \frac{\text{Solvent in Rest}}{\text{Solvent in L.P.}} \times \text{(NH}_4\text{)}_2\text{SO}_4 \text{ in L.P.} \\ &= N \end{aligned}$$

$$\begin{aligned} \text{(NH}_4\text{)}_2\text{SO}_4 \text{ present in true} \\ \text{solid phase.} &= \text{(NH}_4\text{)}_2\text{SO}_4 \text{ in Rest} - N \\ &= N_s \end{aligned}$$

Percentage composition of the true solid phase is given by

$$\text{H}_2\text{SO}_4 = \frac{F_s \times 100}{F_s + N_s} \text{ per cent.}$$

$$\text{(NH}_4\text{)}_2\text{SO}_4 = \frac{N_s \times 100}{F_s + N_s} \text{ per cent.}$$

From this the formulae $x(\text{NH}_4)_2\text{SO}_4, y\text{H}_2\text{SO}_4$ can be determined in the ordinary way and are shown in the last columns of Tables I and II.

Unlike sodium hydrogen sulphate, ammonium hydrogen sulphate shows no sign of gel formation when treated with alcoholic sulphuric acids of any concentration. The solid products obtained were of a definitely crystalline appearance, as if formed from solution. With alcoholic sulphuric acids of 80 percent. and over the solid phase disappeared. If this liquid is cooled to -18°C and stirred or violently shaken, no solid phase appears. It is possible that the ester has a peptising effect above certain concentrations or the solution may be supersaturated. There seems to be no justification for claiming the existence of a compound of the formula $3(\text{NH}_4)_2\text{SO}_4, 2\text{H}_2\text{SO}_4$. The results obtained which gave roughly that composition can easily be accounted for as mixtures or incomplete transformation. In this work there is evidence of the existence of a compound of the formula $2(\text{NH}_4)_2\text{SO}_4, \text{H}_2\text{SO}_4$ first ob-

served by J. Kendall and M. L. Langdon¹ in the system: $(\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ but the compound $(\text{NH}_4)_3\text{SO}_4, 3\text{H}_2\text{SO}_4$ mentioned by them does not appear in the system.

Summary and Conclusions

1. The establishment of equilibrium in the system $(\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{SO}_4 - \text{C}_2\text{H}_5\text{O}$ is more rapid than in the case of the corresponding system with sodium sulphate.

2. The solid $3(\text{NH}_4)_2\text{SO}_4, \text{H}_2\text{SO}_4$ formed by the action of alcohol on ammonium hydrogen sulphate $(\text{NH}_4)_2\text{SO}_4, \text{H}_2\text{SO}_4$ is amorphous, but the solid phases obtained by the action of alcoholic sulphuric acids on ammonium hydrogen sulphate are crystalline. From this it appears that the solid phase separates from solution.

When the liquid phase contains:

| | |
|----------------------------------|----------------|
| Total acidity | 3.28 to 17.23% |
| H_2SO_4 as ester | 0.28 to 2.53% |
| "Free" H_2SO_4 | 2.72 to 12.77% |

the solid phase is $3(\text{NH}_4)_2\text{SO}_4, \text{H}_2\text{SO}_4$.

3. In the interaction of alcohol with ammonium hydrogen sulphate when the ratio

$$\frac{\text{weight of ammonium hydrogen sulphate}}{\text{weight of alcohol}}$$

is about unity or greater than unity there are indications that a hydrogen sulphate of the formula $2(\text{NH}_4)_2\text{SO}_4, \text{H}_2\text{SO}_4$ is formed. This solid phase is not produced when alcoholic sulphuric acids act upon ammonium hydrogen sulphate. This is probably due to the presence of ester in the alcoholic sulphuric acid. Since extraction of sulphuric acid from the ammonium hydrogen sulphate is rapid and precedes esterification and the esterification proceeds slowly², there is, in the early stages of the reaction, a higher concentration of free sulphuric acid than ever exists in the alcoholic sulphuric acid of corresponding total acidity used for interaction with the ammonium hydrogen sulphate. It should be observed, however, that when the percentage of free acidity in the alcoholic sulphuric acid is such that, on these grounds the compound $2(\text{NH}_4)_2\text{SO}_4, \text{H}_2\text{SO}_4$ might be expected the solid phase is the hydrogen sulphate, NH_4HSO_4 .

4. When the liquid phase contains:

| | |
|----------------------------------|-----------------|
| Total acidity | 18.13 to 22.22% |
| H_2SO_4 as ester | 3.08 to 4.37% |
| "Free" H_2SO_4 | 11.97 to 13.48% |

the solid phase gives the composition $3(\text{NH}_4)_2\text{SO}_4, 2\text{H}_2\text{SO}_4$.

It is doubtful if there is sufficient evidence on which to claim the existence of a compound of this formula. The results corresponding roughly with the

¹ J. Am. Chem. Soc., 42, 2138 (1920).

² Dunicliff: J. Chem. Soc., 123, 477 (1923).

composition can easily be accounted for on the bases of incomplete action and there is no definite break in the curve which would correspond with the appearance of this phase.

5. When the liquid phase contains:

| | |
|-----------------------------------------|-----------------|
| Total acidity | 24.45 to 66.63% |
| H ₂ SO ₄ as ester | 5.48 to 12.06% |
| Free H ₂ SO ₄ | 13.49 to 42.51% |

the solid phase is (NH₄)₂SO₄, H₂SO₄.

Dunncliff has shown by the extraction method (vide Table I, footnote) that ammonium sulphate when acted upon with 51-81% alcoholic sulphuric acid yields the solid phase (NH₄)₂SO₄, H₂SO₄. These results roughly correspond as with the proportions used in the latter experiments recorded in Table II. The alcoholic sulphuric acid of 81% strength would be reduced to a lower total acidity owing to the loss of sulphuric acid from the liquid phase to the ammonium sulphate in forming ammonium hydrogen sulphate.

6. When alcoholic sulphuric acids having a total acidity of 80% or over interact with ammonium hydrogen sulphate, the solid disappears and no solid phase separates at -18°C. This is probably due to the great solubility of the salt in concentrated acids or to peptisation due to the presence of alcohol and ethyl hydrogen sulphate. The acid salt¹ (NH₄)₂SO₄, 3H₂SO₄ (H₂SO₄ = 69%) m.p. 48° does not appear in this system even when 90% alcoholic sulphuric acid containing 72% free H₂SO₄ is used.

7. The results indicated by the phase diagram developed, employing as components: (NH₄)₂SO₄ - free H₂SO₄ - (EtHSO₄ + H₂O + C₂H₅OH) show that the equilibrium depends on some factor or factors other than the concentration of free H₂SO₄. Attempts to develop a diagram in which the concentration of ethyl sulphuric acid was taken into consideration gave results which were even less definite than those reported in this paper.

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¹ Kendall and Landon: J. Am. Chem. Soc., 42, 2138 (1920).

LITHIUM CHLORIDE AMMONIA COMPLEXES

BY S. C. COLLINS AND F. K. CAMERON

Introduction

From the literature it appears that lithium chloride absorbs ammonia to form a series of definite compounds containing one mole lithium chloride (LiCl) to one, two, three, four, five or six and one half moles of ammonia (NH₃). Bonnefoi¹ reports preparing the one, two, three and four ammonia complexes by passing ammonia, at atmospheric pressure, over dry lithium chloride. The stable solid formed at 85°C is monammonio-lithium chloride (Li.Cl.NH₃). Below 85°C and above 60°C the stable solid is the di-ammonio-lithium chloride, according to Bonnefoi; between 60°C and 15°C the tri-ammonio and below 12°C the tetra-ammonio-lithium chloride is the stable solid. Between -45°C and -78.5°C, Bilby and Hausen² found as stable solids the quinta-ammonio-lithium chloride and the complex containing one mole lithium chloride to six and one half moles ammonia. Ephraim³ confirmed the existence of the tetra-ammonio-lithium chloride, finding its vapor pressure to be 760 mm. at 12°C. In the present investigation, the possible existence of the di-ammonio-complex is not confirmed, although many efforts have been made to obtain it. Nor do the vapor pressure measurements for monammonio-lithium chloride accord with those of Bonnefoi. It has been found that, at temperatures between 20°C and 30°C monammonio- and tri-ammonio-lithium chlorides are stable in the presence of water.

Materials

The lithium chloride was prepared by dissolving "Baker's Analyzed," strongly acidifying the solution with hydrogen chloride and recrystallizing. The ammonia was taken directly from a cylinder of commercial liquid ammonia, there being no volatile components present which might interfere with the formation of the ammonio-lithium chloride complexes.

The System: Lithium Chloride-Ammonia

Attempts to dry lithium chloride by heating it in the absorption flask resulted in a dense cake with a glazed surface very poorly adapted to the absorption of ammonia. The difficulty was overcome by immersing the flask in a bath at 180°C while dry ammonia was passed through the flask. There is no absorption of ammonia at this temperature. The ammonia was dried by passing it through a train consisting of a four-foot tube containing flakes of sodium hydroxide, a second four-foot tube containing chips of metallic sodium and finally, an eight-inch column of molten metallic sodium. That

¹ Ann. Chim. Phys., (7) 23, 317 (1901).

² Z. anal. Chem., 127, 1 (1923).

³ Ber., 52, 236 (1919).

the drying of the lithium chloride was completed was determined by the flask coming to constant weight, and the content of lithium chloride was then known quite accurately. The flask was suspended in ice water and dry ammonia passed through until there was no further absorption, the process requiring ten to twelve hours.

Four trials were made in this way and in each case there were absorbed four moles of ammonia (NH_3) per mole of lithium chloride (LiCl), thus confirming Bonnefoi's results. Also, a determination of the vapor pressure at 0°C accorded perfectly with that of Bonnefoi. On standing at room temperature for a few hours, the tetra-ammonia complex loses exactly one mole of ammonia. And when the dry lithium chloride is brought into contact with the dry ammonia at room temperature, again the stable solid persisting is the tri-ammonio complex. Thus, a sample of the tetra complex kept for some hours at 25°C and then analyzed, gave 2.99 moles NH_3 per mole LiCl .

A number of trials were made to obtain the complex $\text{LiCl} \cdot 2\text{NH}_3$ by heating the tri-ammonio complex to 60°C . Always, two moles of ammonia escaped, leaving the monammonio complex, $\text{LiCl} \cdot \text{NH}_3$. Similarly a sample of the tetra-ammonio complex heated to 66.4°C gave a residue which, on analysis, yielded 0.992 moles ammonia per mole lithium chloride. Bonnefoi states: "*LiCl \cdot 2NH_3 se produit toutes les fois que l'on fait absorber NH_3 par LiCl entre 60° et 88°, ou bien en maintenant les composés LiCl \cdot 3NH_3, ou LiCl \cdot 4NH_3, entre ces deux températures.*" Hence, further efforts were made by causing lithium chloride to absorb ammonia between 60°C and 85°C , but in no case was the di-ammonio complex obtained. Typical analyses of the products obtained by absorption of ammonia, in moles per mole lithium chloride, gave 3.97 at 0°C , 2.93 at 23°C , and 0.99 at 64°C .

Isotherms, showing the successive pressures as ammonia is removed from these complexes, were determined; and, for this purpose, special equipment was designed and gradually assembled until a satisfactory form was developed. Since the accumulation of the data for any one isotherm required a period of several days, during which the temperature of the absorption complex must be kept continually quite constant, a special form of constant temperature bath or thermostat was developed, which has already been described.¹ Various experimental difficulties, particularly leakage of ammonia kept long in contact with stop-cocks and rubber joints, and corrections for meniscus in tubes and vessels of various diameters, were finally eliminated in the assembly illustrated in Fig. 1. A long-necked flask, A, of Pyrex, to contain the lithium chloride, carries a two-hole rubber stopper, cut to fit very snugly and crowded far down the neck. Above the stopper mercury forms a seal. The glass tubes B and B' are 4 mm. in diameter, without joints and terminate in mercury wells, C and C'. C is an extraction thimble, fitted closely with a stopper carrying, besides the tube B, another bent tube of the same diameter, E, carrying the mercury at atmospheric level to the scale, for comparison with the mercury in B. Being of the same diameter, com-

¹ S. C. Collins: J. Phys. Chem., 31, 1097 (1927).

parison can be directly made without correction for meniscus or capillarity. The Gooch funnel, C', forms a trap through which ammonia can be drawn without breaking the seal, and is fitted with a mercury reservoir D, for which an ordinary separatory funnel serves. The closely fitting stopper carries a tube with accurately ground glass stop-cock connecting with the absorption

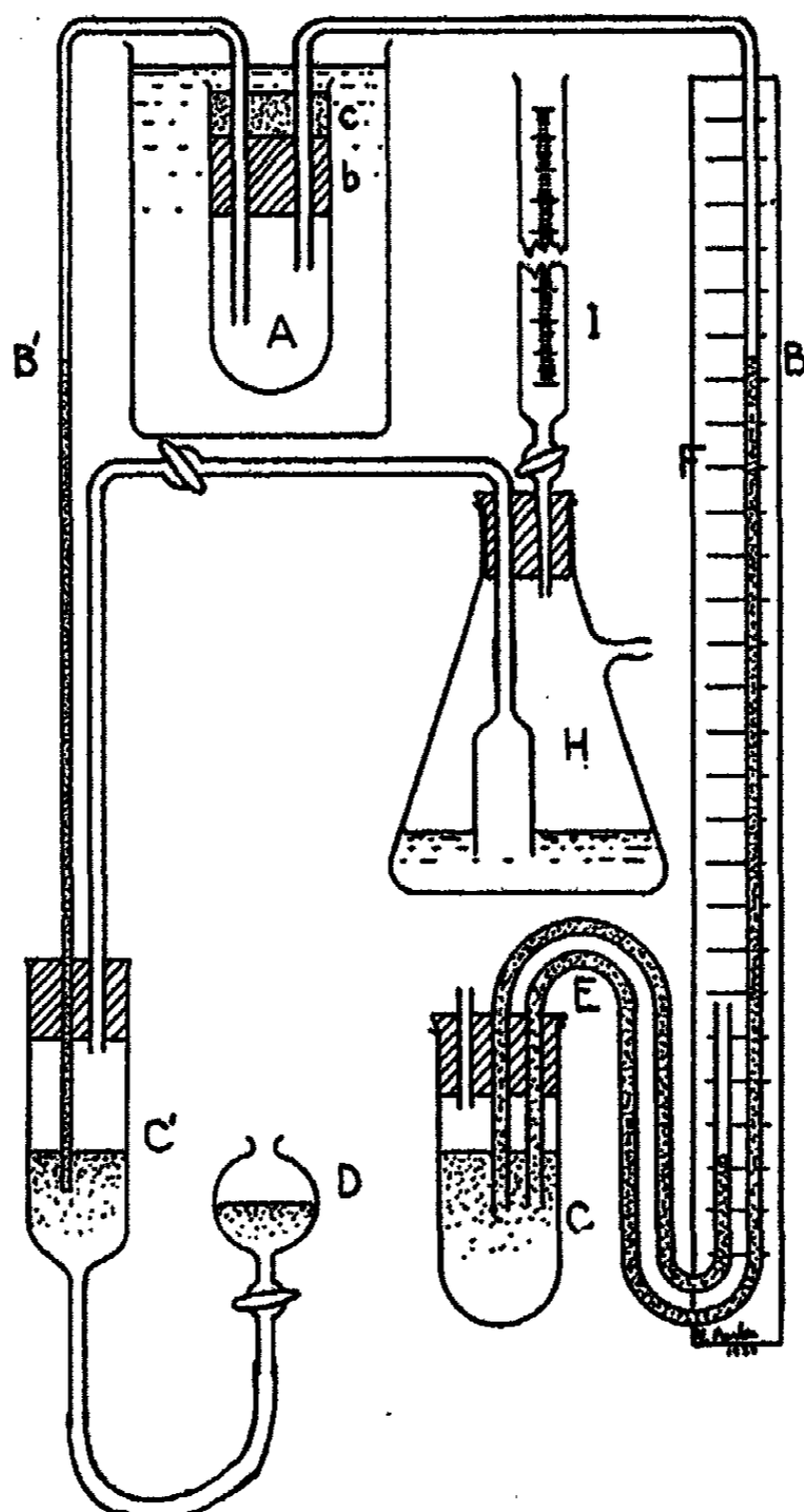


FIG. 1
Apparatus for determining Vapor Pressures.

flask, H, which in turn is fitted with a burette, I, through the stopper as illustrated. The volume of the flask A, together with the two tubes entering it, is approximately 65 cc.

The entry of the two tubes into A permits one to pass dry ammonia over the lithium chloride, contained therein, and prepare the complex desired after assembly is set up. An experiment may be repeated a number of times, without dismantling the assembly. The only outlets being mercury sealed, leak-

age is practically eliminated. A constant temperature in A is maintained by immersing it in the bath as noted above.

An accurately weighed sample of lithium chloride, approximately 2.5 grams, is dried in the flask A, as described above, that is by passing a current of dry ammonia through the flask, while the latter is kept at a temperature of 180°C or higher. The flask is then assembled with the tubes and submerged in the bath at a cool temperature, while dry ammonia passes through the flask for several hours. There is an absorption of ammonia the course of which is followed by bringing the ends of the tubes under mercury from time to time and noting if the mercury rises in the tubes. When

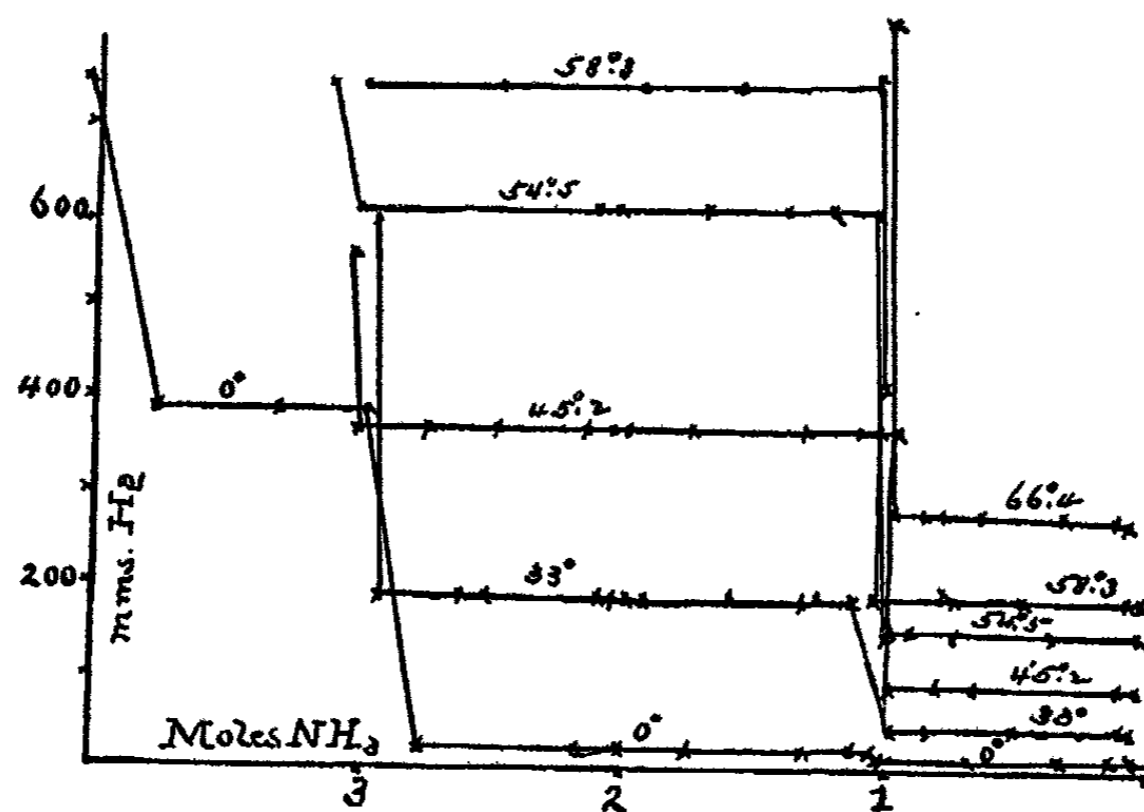


FIG. 2
Vapor Pressure—Concentration Curves for the System: $\text{LiCl}-\text{NH}_3$.

the absorption is completed, the system is brought to the pre-determined temperature and maintained at that temperature continually. The regulator is adjusted and successive small quantities of ammonia are removed by aspirating through standard hydrochloric acid solution and then determined. A vapor pressure reading is made between each removal of ammonia. The total amount of ammonia absorbed in the complex is computed from the sum of the successive small portions removed. The results obtained in several series determined as just described are given in Table I and plotted in Fig. 2. Consider the isotherm for 0°C . There being two components in the system, lithium chloride and ammonia, then with two solid phases in contact with the gas phase (NH_3) the system is, in general, univariant. But, the temperature being fixed, the system becomes invariant, and the pressure remains constant until one of the phases disappears. Thus, starting with tetra-ammonio-lithium chloride, $\text{LiCl}\cdot 4\text{NH}_3$, in equilibrium with gaseous NH_3 and at a pressure of 750 mm. Hg, and keeping the temperature of 0°C , when ammonia is withdrawn, the pressure quickly falls to 387 mm., with the appearance of a

second solid phase, tri-ammonio-lithium chloride, $\text{LiCl} \cdot 3\text{NH}_3$, and the pressure remains constant with subsequent withdrawals of ammonia, until all tetra-ammonio complex disappears. With further withdrawal of ammonia there is an abrupt fall of the vapor pressure to 22 mm. with the appearance of a new solid phase, the monammonio complex. The tri-ammonio complex persists together with the monammonio complex in contact with the gas phase at the constant pressure of 22 mm. until, with successive withdrawals

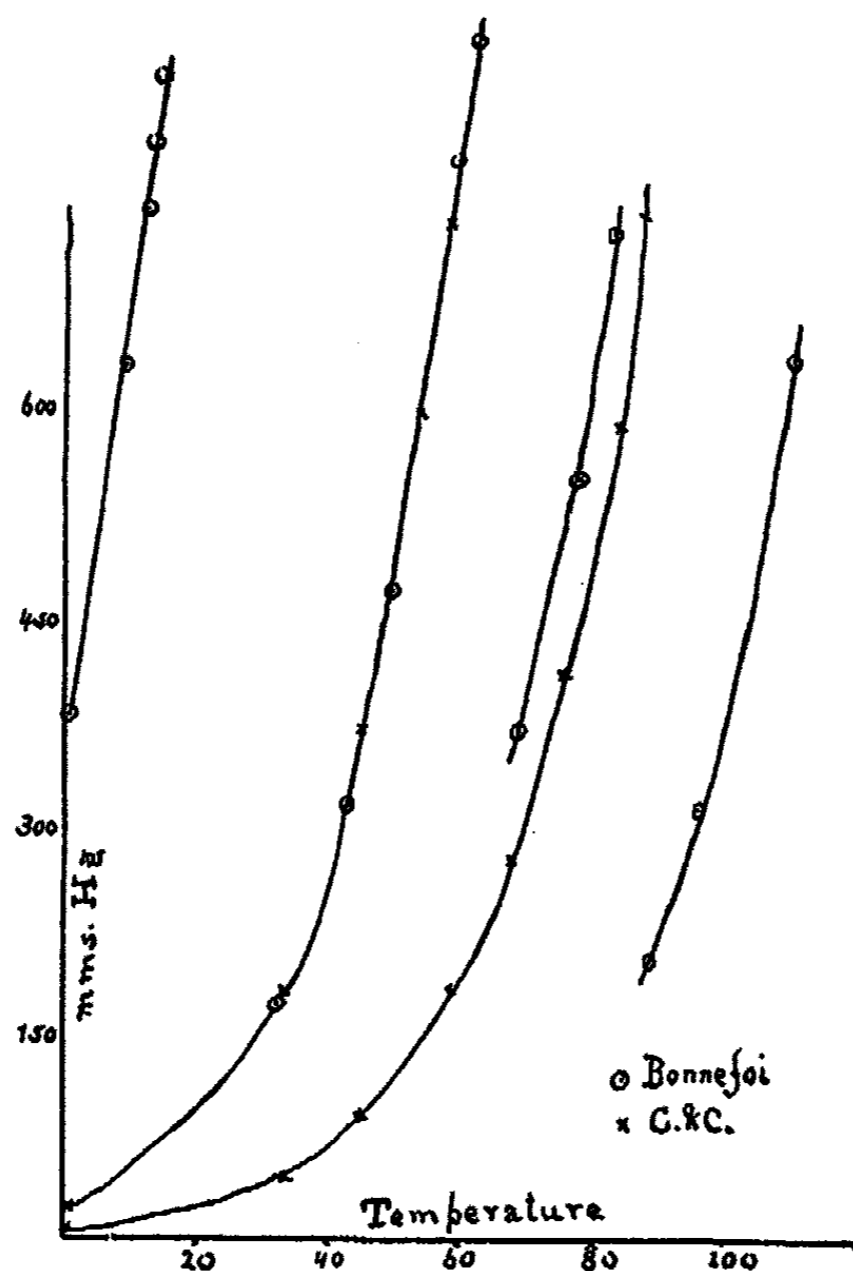


FIG. 3
Vapor Pressure—Temperature Curves for the System : $\text{LiCl}-\text{N H}_3$.

of ammonia, there is no longer sufficient ammonia present to form the tri-ammonio complex. With a further withdrawal of ammonia, there is again an abrupt fall in pressure to 5.5 mm. with the appearance of lithium chloride as one of two solid phases in contact with the gas phase, the other solid phase being, of course, the monammonio complex; and this pressure persists until all of the ammonia is withdrawn from the system, when there is another sudden drop of pressure to a point approximating zero, and the only phase remaining is solid lithium chloride, although theoretically, there is also a gas phase instead of the very complete approach to a vacuum actually realized.

TABLE I
 Vapor pressures in the system: LiCl-NH₃.
 NH₃ in moles per mole LiCl in the system.
 Pressures in mms. Hg.

| 0° | | 33° | | 45.2° | | 54.5° | |
|-----------------|------|-----------------|-------|-----------------|-----|-----------------|-----|
| NH ₃ | mm. | NH ₃ | mm. | NH ₃ | mm. | NH ₃ | mm. |
| 4.01 | 750 | 2.93 | 600 | 3.05 | 556 | 3.1 | 750 |
| 3.75 | 387 | 2.9 | 185.8 | 3.01 | 368 | 2.99 | 611 |
| 3.30 | 387 | 2.6 | 185.8 | 2.98 | 372 | 2.1 | 612 |
| 2.98 | 366 | 2.5 | 185.8 | 2.75 | 372 | 1.7 | 611 |
| 2.75 | 28.0 | 2.3 | 185.8 | 2.48 | 372 | 1.4 | 611 |
| 2.15 | 22.0 | 2.05 | 185.8 | 2.15 | 372 | 1.21 | 611 |
| 1.99 | 22.0 | 1.97 | 185.8 | 2.03 | 372 | 1.05 | 611 |
| 1.75 | 22.0 | 1.9 | 185.8 | 1.99 | 372 | .98 | 156 |
| 1.30 | 22.0 | 1.6 | 185.8 | 1.75 | 372 | .90 | 152 |
| 1.10 | 22.0 | 1.3 | 185.8 | 1.30 | 372 | .75 | 149 |
| 1.04 | 20.0 | 1.25 | 185.8 | 1.10 | 372 | .38 | 152 |
| 1.00 | 6.0 | 1.03 | 185.8 | 1.04 | 372 | .04 | 151 |
| .65 | 5.5 | .99 | 92.0 | 1.00 | 372 | .00 | 0 |
| .35 | 5.5 | .97 | 47.5 | .99 | 371 | | |
| .05 | 5.5 | .83 | 47.5 | .97 | 126 | | |
| .00 | 0.0 | .51 | 47.5 | .80 | 92 | | |
| | | .10 | 46.0 | .65 | 92 | | |
| | | .05 | 47.0 | .35 | 92 | | |
| | | .00 | 0.0 | .05 | 92 | | |
| | | | | .00 | 0 | | |

| 58.3° | | 66.4° | | 74.9° | | 86.9° | |
|-------|-------|-------|-----|-------|-----|-------|-------|
| 2.98 | 745.5 | 1.02 | 755 | 0.81 | 423 | 0.85 | 750.5 |
| 2.47 | 745.5 | 1.00 | 420 | | | 0.66 | 750.5 |
| 1.95 | 745.5 | .99 | 281 | | | | |
| 1.60 | 745.5 | .97 | 281 | | | | |
| 1.03 | 745.5 | .85 | 281 | | | | |
| 1.00 | 358.0 | .66 | 285 | | | | |
| .99 | 189.0 | .60 | 282 | | | | |
| .75 | 185.0 | .33 | 282 | | | | |
| .47 | 185.0 | .14 | 282 | | | | |
| .10 | 185.0 | .08 | 274 | | | | |
| .00 | .0 | .00 | 0 | | | | |

| 82° | |
|------|-----|
| 0.81 | 598 |

In a similar way, and quite as sharply, the data obtained define the isotherms for 33° , 45.2° , 54.5° , and 58.3° C, commencing with the removal of ammonia from a system of tri-ammonio-lithium chloride in contact with gaseous ammonia. The tetra-ammonio complex is not stable at these temperatures at the pressure of an atmosphere. The data obtained at 66.4° leave no reasonable doubt that at that temperature, the only stable complex is the monammonio-lithium chloride.

Since there was, relatively, a fairly large volume of gas phase in contact with the mixture of solids in the absorption flask and connections, data were realized for a few points on the vertical portions of the isotherms, these vertical sections being pressure-volume curves for the gas remaining in the flask during the transition from a system with a high pressure level to the system with the lower pressure level.

From the data in Table I the pressure-temperature relations are plotted in Fig. 3, and for convenience in comparison also the data of Bonnefoi. The data for the tetra- and tri-ammonio complexes are in very satisfactory accord. The data for monammonio lithium chloride yield a curve almost coinciding with one plotted from Bonnefoi's data for the di-ammonio complex. It might be assumed that Bonnefoi obtained the di-ammonio complex as an unstable solid, since the data here reported show the monammonio complex to be stable over the temperature-pressure range concerned. But if the data here reported for the mono complex be correct, the question arises as to what was the complex which Bonnefoi supposed to be the mono complex. Possibly it was another modification. Roozeboom¹ cites a case where a hydrate exists in two modifications with two different vapor tensions for each particular temperature. Jänecke² has shown in the system $K_2PO_4 - H_2O - NH_3$, within temperatures from 0° C to 25° C, at least, there can exist two liquid phases in contact with a gas phase, so that metastability may be anticipated in systems in which ammonia is a component. But Bonnefoi's modification of the monammonio complex should be more stable than the one obtained in the present investigation. The results of the present investigation are offered with confidence that they are approximately correct in absolute magnitudes and that they do represent stable equilibrium conditions.

The System: Lithium Chloride-Ammonia-Water

A series of solutions was prepared of varying concentrations with respect to ammonia, and with lithium chloride present in excess. When it appeared that equilibrium had been attained, analyses of the clear liquid phase and of the corresponding residue of liquids and solids were made, the results being assembled in Table II. When plotted on a triangular diagram in the conventional way, Fig. 4, the data indicate that this system yields three solid phases at a temperature of 25° , namely, lithium monohydrate ($LiCl \cdot H_2O$) in contact with solutions containing up to 15% ammonia, monammonio-lithium

¹ Z. physik. Chem., 4, 43 (1889).

² Z. physik. Chem., 127, 82 (1927).

chloride ($\text{LiCl}\cdot\text{NH}_3$) in contact with solutions containing from about 15% to somewhat more than 27% ammonia, and triammonio-lithium chloride ($\text{LiCl}\cdot 3\text{NH}_3$) in contact with solutions containing 32% to 40% ammonia.

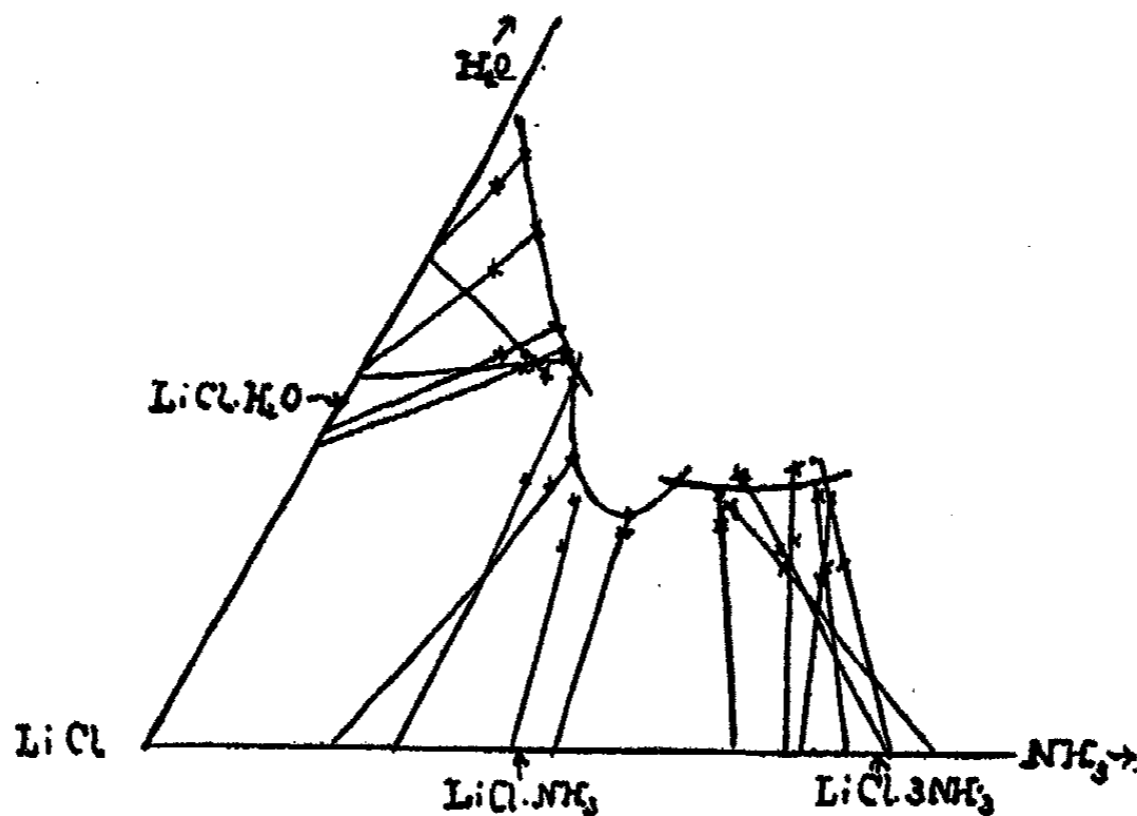


FIG. 4
Isotherms and corresponding Solids for the System: $\text{LiCl}-\text{NH}_3-\text{H}_2\text{O}$, at $23^\circ-25^\circ\text{C}$.

TABLE II
Percentage composition of liquid and of residue in system: $\text{LiCl}-\text{NH}_3-\text{H}_2\text{O}$,
at $23^\circ-25^\circ\text{C}$

| Liquid | | | Residue | | |
|--------|---------------|----------------------|---------|---------------|----------------------|
| LiCl | NH_3 | H_2O | LiCl | NH_3 | H_2O |
| 45.4 | 0.00 | 54.6 | | | |
| 46.7 | 3.1 | 50.2 | 49.5 | 2.5 | 47.9 |
| 48.1 | 7.9 | 44.0 | 54.4 | 5.7 | 39.9 |
| 50.84 | 13.88 | 35.28 | 56.57 | 10.27 | 33.16 |
| 54.90 | 14.16 | 30.94 | 54.52 | 12.41 | 33.07 |
| 50.73 | 14.86 | 34.41 | 53.92 | 12.67 | 33.41 |
| 50.81 | 15.34 | 33.85 | 55.12 | 12.16 | 32.72 |
| 51.9 | 16.70 | 31.4 | 60.0 | 16.5 | 23.5 |
| 54.7 | 20.0 | 25.3 | 58.2 | 19.1 | 22.7 |
| 57.0 | 21.64 | 21.36 | 58.88 | 23.0 | 18.12 |
| 52.57 | 27.31 | 20.12 | 54. | 28.3 | 17.7 |
| 46.1 | 32.0 | 21.9 | 47. | 35.3 | 17.7 |
| 45.3 | 32.7 | 22.0 | 45.1 | 39.3 | 15.6 |
| 41.52 | 35.7 | 22.8 | 44.3 | 41.7 | 14.0 |
| 39.3 | 35.8 | 24.9 | 42.8 | 39.4 | 17.8 |
| 38.28 | 36.53 | 25.29 | 39.95 | 44.21 | 15.64 |
| 39.11 | 38.6 | 22.3 | 41.26 | 43.9 | 14.84 |
| 37.9 | 40.4 | 21.7 | 43.1 | 44.9 | 12.0 |
| 45.9 | 33.2 | 20.9 | 45.3 | 39.6 | 15.1 |

The data in Table III (charted in Fig. 5) were calculated from Table II. The corresponding numbers in the two columns indicate the amounts in moles of ammonia and of lithium chloride respectively that will jointly dissolve in 100 grams of water. The curves in Fig. 5 show that there is a steady increase in the amount of lithium chloride dissolved in water when ammonia is added until there is present a mole of ammonia per mole of lithium chloride. At this point monammonio-lithium chloride becomes the stable solid phase. Con-

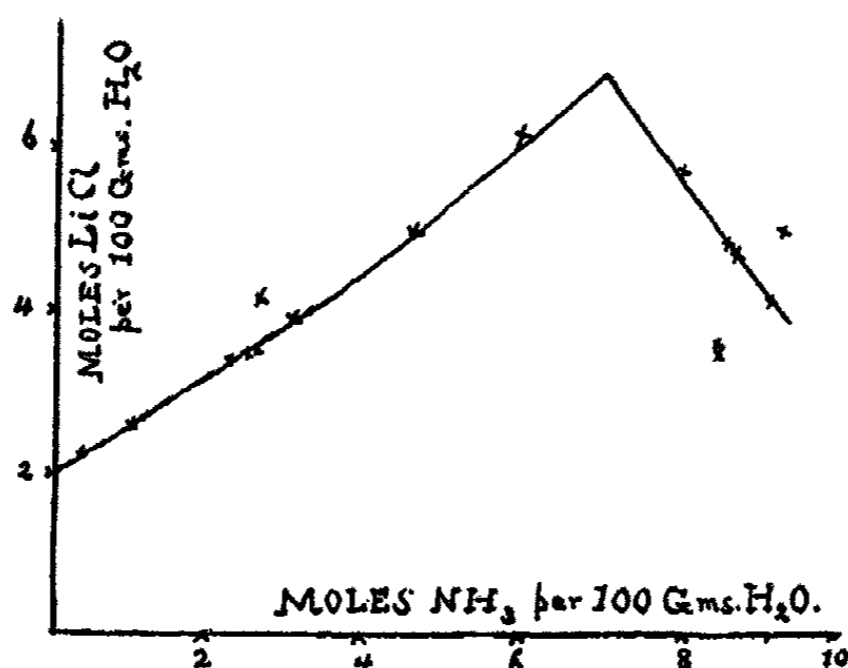


FIG. 5
Mutual Solubilities of Lithium Chloride and Ammonia in Water at 23°-25°C.

TABLE III

Mutual solubility of Lithium Chloride and Ammonia in Water. Moles solute per 100 grams water. Temperature 23°-25°C

| NH ₃ | LiCl | NH ₃ | LiCl | NH ₃ | LiCl |
|-----------------|------|-----------------|------|-----------------|------|
| 0.00 | 1.96 | 2.70 | 4.19 | 8.49 | 3.58 |
| 0.36 | 2.19 | 3.12 | 3.90 | 8.59 | 4.99 |
| 1.05 | 2.58 | 4.65 | 5.09 | 8.73 | 4.87 |
| 2.32 | 3.40 | 5.97 | 6.30 | 9.20 | 4.29 |
| 2.53 | 3.47 | 7.98 | 5.88 | 9.35 | 5.19 |
| 2.66 | 3.53 | 8.47 | 3.73 | | |

tinued addition of ammonia to a high concentration precipitates a solid phase which, as pointed out in the preceding paragraph, seems to be the triammonio-lithium chloride.

The existence of the above cited solid phases in contact with the solutions was confirmed by vapor pressure measurements made with the apparatus shown in Fig. 1. In these experiments a relatively large proportion of the solid phase was present, a condition attained by first preparing triammonio-lithium chloride in the reaction chamber A, and then adding water. Vapor pressure readings were made between each withdrawal of ammonia. The results are assembled in Table IV and charted in Fig. 6.

The addition of a small amount of water increases the vapor pressure of the mixture. But it is only that part of the solid which dissolves that is affected, for, the less the water added, the smaller the amount of gaseous ammonia that must be withdrawn before the pressure falls to the value due

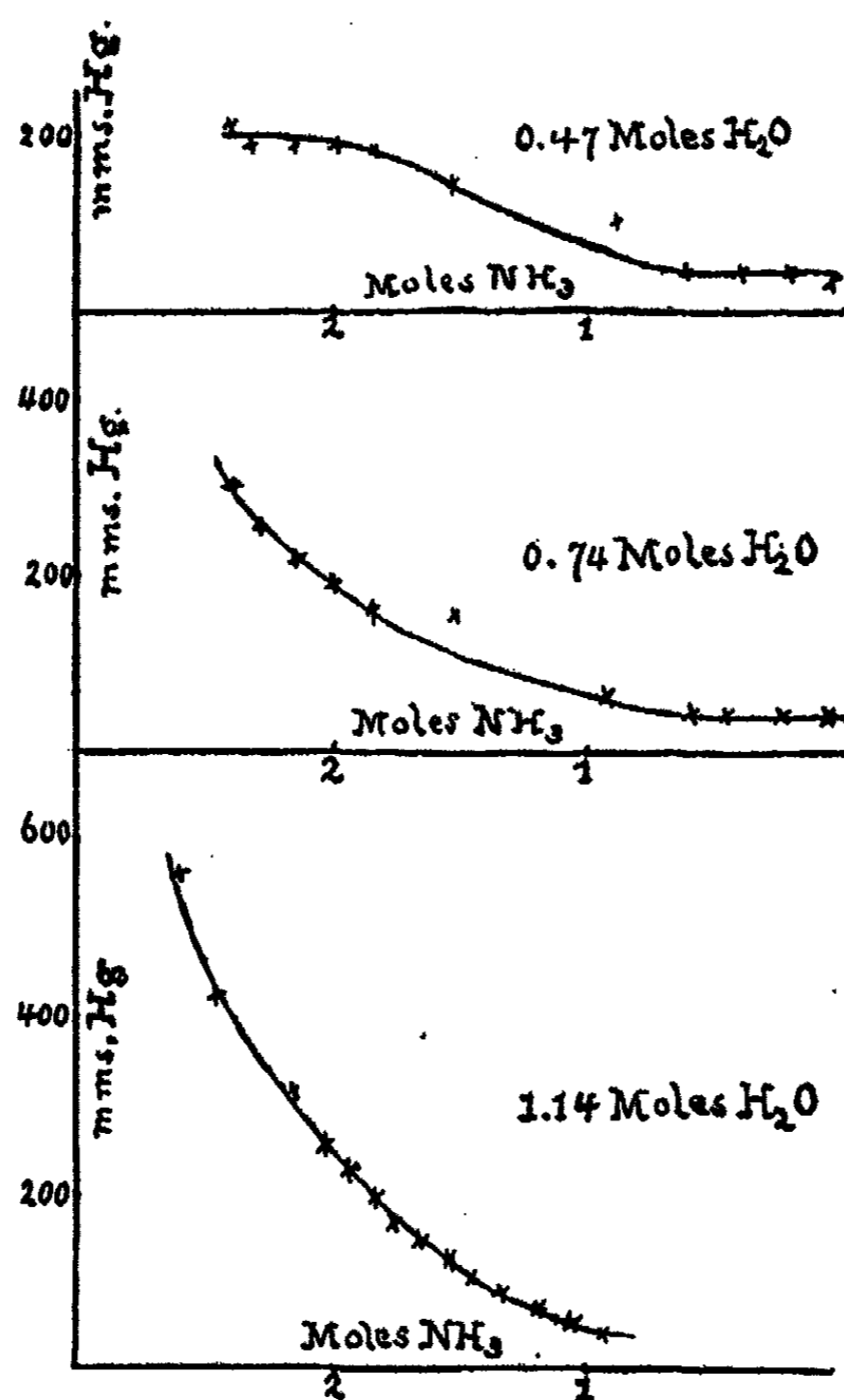


FIG. 6

Vapor Pressure—Concentration Curves at 25°C for the System : LiCl—NH₃—H₂O.
Solid Phases, LiCl₃NH₃, LiCl.NH₃, and LiCl.H₂O

to the dry complex. After bringing about the reaction with the liberation of a certain amount of ammonia from the complex, the further effect of the water is analogous to greatly increasing the volume of the container. Thus, there is significance in the sections of the pressure-concentration isothermals lying between the horizontal sections. The more water present, the greater the "effective" volume of the system and the less abrupt the change in pressure with the disappearance of one solid phase and the appearance of another.

TABLE IV
Vapor pressures for the system: LiCl-NH₃-H₂O, Temperature 25°C

| Moles NH ₃ per Mole LiCl | Moles H ₂ O per Mole LiCl | | | Moles NH ₃ per Mole LiCl | Moles H ₂ O per Mole LiCl | | |
|-------------------------------------------|--------------------------------------|----------------|----------------|-------------------------------------------|--------------------------------------|----------------|----------------|
| | 0.47 mm. Hg | 0.74 mm. Hg | 1.14 mm. Hg | | 0.47 mm. Hg | 0.74 mm. Hg | 1.14 mm. Hg |
| 2.69 | | | 738 | 1.62 | | | 149 |
| 2.59 | | | 568 | 1.51 | | | 122 |
| 2.45 | | | 428 | 1.5 | 146 | 164 | |
| 2.4 | 212 | 300 | | 1.40 | | | 103 |
| 2.3 | 187 | 258 | | 1.30 | | | 85 |
| 2.2 | 186 | 215 | | 1.16 | | | 68 |
| 2.16 | | | 315 | 1.03 | | | 55 |
| 2.04 | | | 260 | .94 | | | 40 |
| 2.0 | 184 | 190 | | .90 | 111 | 65 | |
| 1.95 | | | 230 | .6 | 45 | 45 | |
| 1.85 | 186 | 165 | | .4 | 46 | 40 | |
| 1.81 | | | 195 | .2 | 44 | 36 | |
| 1.73 | | | 171 | .05 | 25 | 30 | |

The data assembled in Table II and charted in Fig. 4 are far from satisfactory. It was impracticable to obtain truly representative samples for analysis. There was always a loss of ammonia when withdrawing samples of either liquid or residue, since, generally, the solutions were highly charged with this gas. More serious was the impracticability of obtaining residue samples reasonably low in adhering mother liquor. Furthermore, the concentration of lithium chloride in the solutions ranged from 40% to 60%, while the range in the solid phase was from 45% to 70%. Hence there could be no great difference in the analysis of the two. It is evident from the plot that the corresponding samples of mother liquor and residue in no case differed sufficiently to justify an approach to accurate drawing of tie lines. Nevertheless, in view of the supporting evidence just adduced, and the fact that no practicable way of overcoming the experimental difficulties can be realized at present, the data are offered as demonstrating with reasonable certainty that the system presents but three isotherms at 25°C, each corresponding to the solid phase indicated.

Summary

1. Satisfactory apparatus has been developed for studying vapor pressures in the systems: lithium chloride-ammonia and lithium chloride-ammonia-water.
2. Vapor pressure measurements for these systems have been tabulated for wide ranges of temperature and concentration.
3. It has been shown that, in the system lithium chloride-ammonia, at temperatures from 0°C to 66°C either tetra-, tri- or monammonio-lithium chloride may be formed. And the pressure-temperature limits for the existence of each have been determined.

4. Vapor pressure measurements for tetra- and tri-ammonio complexes with lithium chloride accord well with measurements by Bonnefoi. Measurements for the monammonio complex do not agree with the published results by Bonnefoi.

5. No evidence could be found for the existence of a diammonio-lithium chloride described by Bonnefoi.

6. It has been shown that in the system: lithium chloride-ammonia-water, either lithium chloride monohydrate, monoammonio-lithium chloride, or triammonio-lithium chloride may be a stable solid phase. The pressure-temperature-concentration limits for the existence of each have been approximated. No evidence was found for the possible existence of a diammonio complex.

7. The significance of the graphs for various isotherms has been discussed.

8. The effect of varying concentrations of ammonia on the solubility of lithium chloride at 25° has been determined.

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THE PREPARATION OF A LEAD SULPHIDE HYDROSOL AND ITS COMBINATION WITH PHOSPHATE IONS¹

BY J. BROOKS

The present paper describes (a) the preparation of a colloidal solution of lead sulphide, and (b) measurements of the rate of combination of the colloid particles with phosphate ions. It was necessary that the sol² should (1) contain a fairly high concentration of colloid (up to 0.5 per cent lead as lead sulphide), (2) be free from any but negligible amounts of ionic lead, (3) be stable on boiling in the presence of one per cent sodium chloride.

Preparation of the Sol

A stream of H₂S was led into a stirred solution (300-400 revs. per min.) of lead acetate containing 0.5 per cent gelatin. After the passage of excess hydrogen sulphide sufficient N. NaHCO₃ was added to neutralise the acetic acid present. Excess H₂O was then removed by passing nitrogen through the boiling sol.³ Coarse particles of PbS were removed by centrifuging and the lead concentration estimated by the method of Fairhall et al.⁴ The sol remained stable indefinitely; it appeared black in thick layers, and the particles were negatively charged. The ultrafiltrate (pH ca. 7.0) contained a negligible amount of ionic lead.

The amounts of colloid formed depended on the initial concentration of lead acetate. Above a certain concentration, the fraction converted into colloid decreased sharply, the lead sulphide being mainly in the form of coarse flocks. The results which were reproducible to within 5 per cent are given in Table I and Fig. 1. Gelatin from the same sample was used throughout and the conditions were uniform.

TABLE I

| Grms. lead per 100 cc. | | Per cent conversion into colloid | |
|-------------------------|----------------------------------|----------------------------------|------------|
| Initial as lead acetate | Final as colloidal lead sulphide | Observed | Calculated |
| 0.25 | 0.24 | 97 | 99 |
| 0.50 | 0.48 | 96 | 96 |
| 0.75 | 0.66 | 88 | 86 |
| 1.0 | 0.52 | 52 | 59 |
| 1.25 | 0.26 | 21 | 26 |
| 1.50 | 0.11 | 7 | 6 |
| 1.75 | 0.05 | 3 | 1 |

¹ This investigation was undertaken on behalf of the Liverpool Medical Research Organization, Director: Professor W. Blair Bell of the University of Liverpool.

² On account of its possible use as a therapeutic agent.

³ It was necessary to neutralise the acetic acid as continued removal of H₂S at 100° in presence of acetic acid resulted in the formation of appreciable amounts of ionic lead.

⁴ "Medicine Monographs," 7, 25 (1926).

The results resemble those obtained in the preparation of lead selenide by a similar method¹ and can be explained on a similar basis. With lead selenide it was shown that the decreased colloid formation in a concentrated lead acetate solution was due to the increased concentration of acetate ion (and acetic acid into which it is transformed). Since the colloid particles when

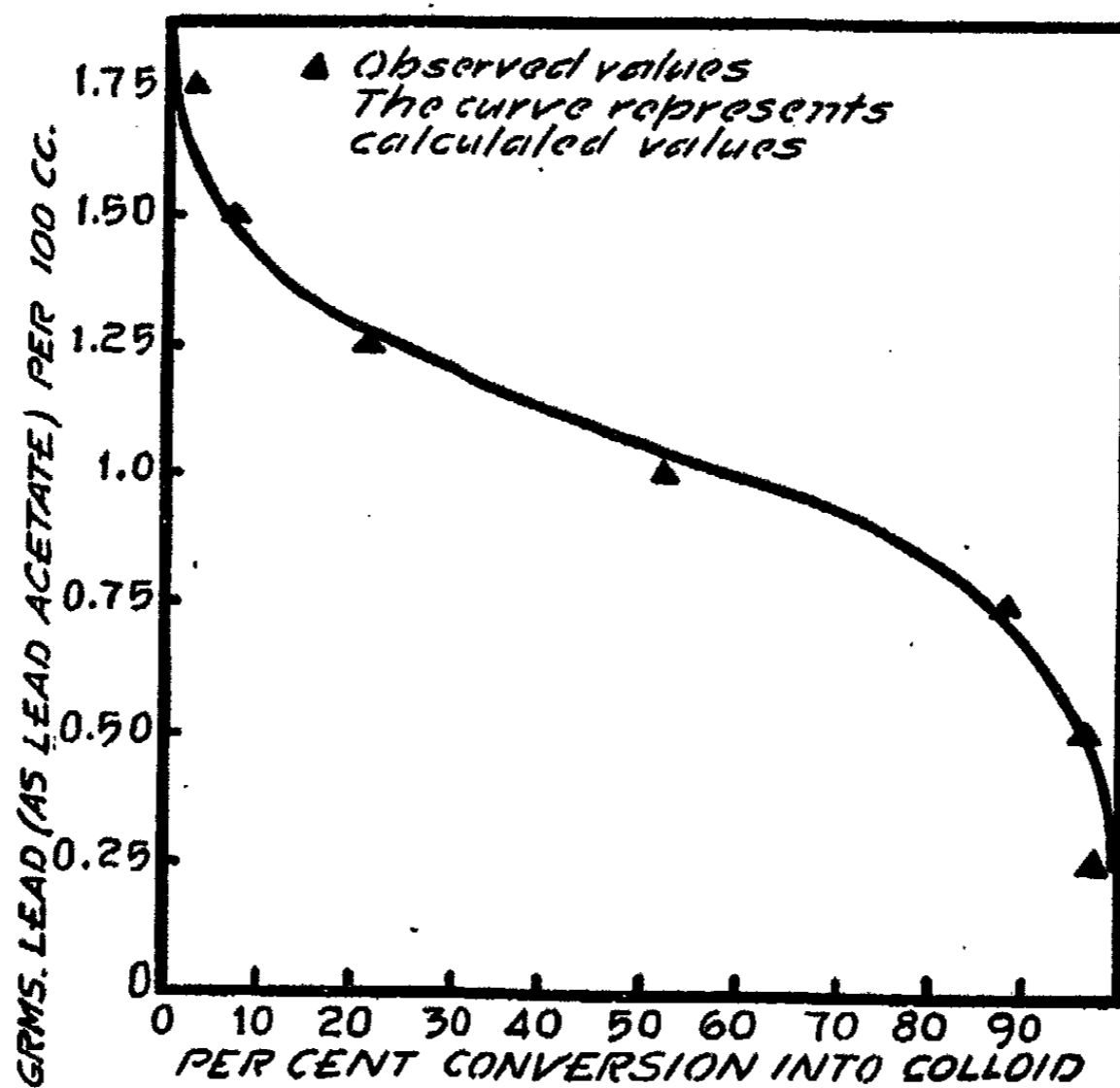


FIG. 1

once formed could not be flocculated by any concentration of sodium acetate, lead acetate or acetic acid the effect was exerted during formation of the sol. It was suggested that acetate ion and acetic acid reduced the velocity of formation of lead selenide nuclei without affecting the velocity of their growth.² The small number of nuclei formed in concentrated solutions of lead acetate would then necessarily grow to large non-colloid particles.

The calculated values in Table I were obtained by the method used in the case of lead selenide. Assuming that in each uncentrifuged sol there are particles of all probable masses it can be shown that the fraction of lead converted into colloid, M_c/M is

$$M_c/M = 1 - e^{-(m_1/\sigma)^2} - (m_1/\sigma)^2 \cdot e^{-(m_1/\sigma)^2}$$

where σ is the most probable particle mass in the sol in question and m_1 is a mass such that all particles of greater mass are removed on centrifuging.

¹ Brooks: J. Phys. Chem., 32, 698 (1928).

² Cf. Hiege: Z. anorg. Chem., 91, 145 (1915).

The values of σ required for the calculation of M_0/M by means of this equation were obtained from a relation which fitted the data of Hiege (*loc. cit.*) on the inhibition by an electrolyte of nuclei formation in a gold sol. In the case of lead selenide the relation was

$$\log_e \sigma/\sigma_0 = 4.95 \times 10^{-4} c^{1.89}$$

and in the case of lead sulphide

$$\log_e \sigma/\sigma_0 = 3.73 \times 10^{-6} c^{2.12}$$

where σ_0 is the most probable mass of a particle in the hypothetical case of formation in the absence of the inhibiting substance and c is the total concentration of acetate (acetate ion and acetic acid) present during the formation of the sol. It is of interest that in both cases the effect of acetate enters as a function which is approximately the square of the concentration.

The Rate of Combination of Lead Sulphide Particles with Phosphate Ions

The sol was added to an aqueous phosphate solution in such amounts that excess of phosphate was always present. The mixture was ultra-filtered¹ at intervals and the uncombined phosphate in the ultra-filtrate estimated by Briggs' modification² of the Bell-Doisy colorimetric method. The phosphate solution contained sodium chloride (0.16 M.) and Na_2HPO_4 and KH_2PO_4 in the ratio $\text{Na}_2\text{HPO}_4/\text{KH}_2\text{PO}_4 = 3.5$. Unless otherwise stated, the total concentration of phosphate was 0.0018 M. The pH of this solution was 7.2.

The disappearance of phosphate from the solution was accompanied by a whitening of the black colloid particles. The mean of several final values of

the ratio $\frac{\text{gm. atoms phosphorus combined}}{\text{gm. atoms lead}}$ was 0.65. Since this value does

not differ greatly from that for the sparingly soluble tertiary lead phosphate $\text{Pb}_3(\text{PO}_4)_2$, i.e. 0.67, it may be assumed that the particles are converted into particles of lead phosphate. The pH increases during the reaction which is therefore probably



Any oxidation of HS' by dissolved oxygen would also increase the pH



Two series of experiments were carried out at 15° C. Volumes of the same sol (Pb content = 0.512 per cent) were added to solutions containing different concentrations of total phosphate. The values of the ratio $\frac{\text{gm. atoms phosphorus combined}}{\text{gm. atoms lead}}$ (denoted by P/Pb) are given in Tables

II and III and Fig. 2. The times are reckoned from the time of mixing to the mid-time of ultra-filtration.

¹ For experimental details, cf. Brooks: *Biochem J.*, 21, 766 (1927).

² *J. Biol. Chem.*, 59, 255 (1924).

TABLE II

5 cc. PbS sol = 25.6 mg. Pb.
100 cc. phosphate solution.
 $t = 15^{\circ} \text{C}$

| Phosphate concentration Time (hours) | 0.0018 M. | | 0.0014 M. | | 0.0009 M. | |
|-----------------------------------------|-----------|--------|-----------|--------|-----------|--------|
| | P/Pb | k | P/Pb | k | P/Pb | k |
| 27 | 0.27 | 0.0051 | 0.25 | 0.0047 | 0.24 | 0.0045 |
| 48 | 0.45 | 0.0057 | 0.39 | 0.0047 | 0.40 | 0.0049 |
| 98 | 0.63 | 0.0054 | 0.63 | 0.0057 | 0.62 | 0.0051 |
| 170 | 0.67 | | 0.66 | | 0.66 | |

TABLE III

10 cc. PbS sol = 51.2 mg. Pb.
100 cc. phosphate solution.
 $t = 15^{\circ} \text{C}$

| Phosphate concentration Time (hours) | 0.0018 M. | | 0.0025 M. | |
|-----------------------------------------|-----------|--------|-----------|--------|
| | P/Pb | k | P/Pb | k |
| 26 | 0.23 | 0.0046 | 0.24 | 0.0049 |
| 47 | 0.36 | 0.0045 | 0.36 | 0.0045 |
| 97 | 0.53 | 0.0041 | 0.55 | 0.0044 |
| 200 | 0.63 | | 0.63 | |

In the experiments in Table II, there was no sedimentation of the particles during the period of the reaction, and slight sedimentation after approximately 200 hours. When twice the amount of colloid was present (Table III) there was slight sedimentation after approximately 80 hours. The pH of the mixtures increased to ca. 9.5 during the reaction.

The rate of transformation into lead phosphate is slow in comparison with the rate of diffusion of phosphate ions to the surface of the particle.¹ It will be seen from Fig. 2 that for a given amount of colloid the rate of transformation is independent of the phosphate concentration within the range investigated. There is therefore no formation of a difficultly permeable layer of lead phosphate round each particle as in such a case the rate of penetration of the coating would be proportional to the phosphate concentration.

¹ If the rate of diffusion of phosphate were the governing process, the velocity of reaction would be represented by the Nernst-Brunner equations, *Z. physik. Chem.*, 47, 52, 56 (1904).

$$\frac{dx}{dt} = k_1(c - x) \quad (a)$$

$$k_1 = D\omega/V\delta \quad (b)$$

where (c - x) = concentration of uncombined phosphate at time t.
D = diffusion constant of the phosphate ion.
 δ = thickness of the diffusion layer.
V = volume of mixture
 ω = area of surface

A mean value of k_1 was obtained from the results in Table II by means of (a) and substituted in (b). D was taken as 8×10^{-6} cm.²/sec and ω calculated on the assumption of an average radius for a particle of 50μ . As this gave impossibly large volumes (several cms.) for the thickness δ of the diffusion layer round a colloid particle, it may be concluded that the measured rate is slow compared to the rate of diffusion to the surface.

Assuming that the velocity of reaction is proportional only to the surface of unchanged particle we would write

$$dx/dt = k(a - x)^{1/2}$$

where a is the final value of P/Pb and x is the value at time t , whence

$$k = r/t[a^{1/2} - (a - x)^{1/2}]$$

The calculated values of k are given in Tables II and III and are reasonably constant. The relation would not hold if there was any aggregation of the

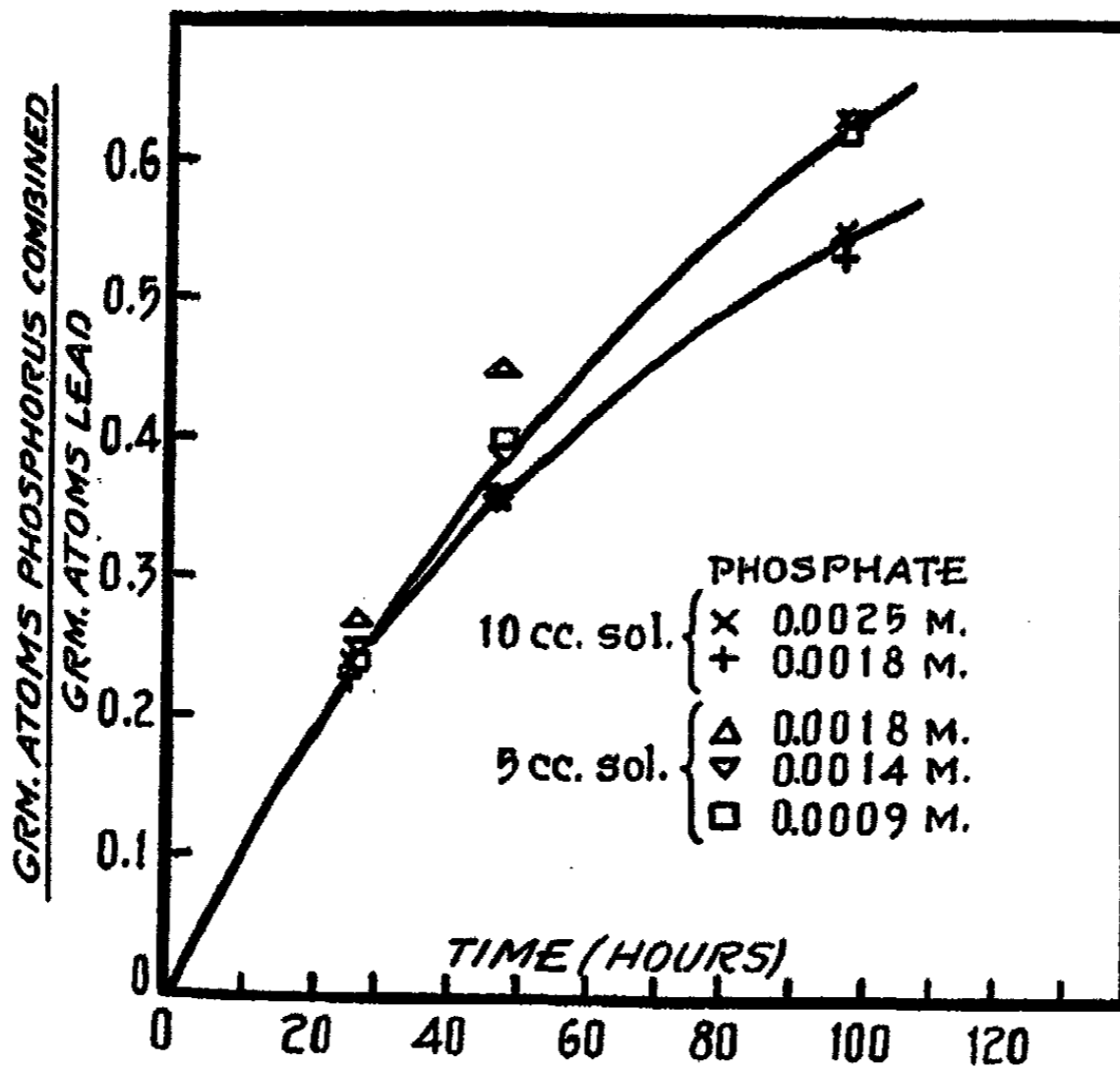


FIG. 2

particles which caused a decrease of reacting surface in addition to the uniform decrease due to combination. The decrease in the values of k in Table III is probably due to slight particle aggregation (v.i.).

Two alternative explanations of the zero order (per unit area) of the reaction may be suggested (a) the reaction takes place slowly between the PbS surface and adjacent adsorbed phosphate ions, and the number of adsorbed ions per unit area is independent of the phosphate concentration over a wide range (the latter is not improbable in the case of ionic adsorption), (b) the measured rate is the slow evaporation of a poison from the surface,¹ e.g. a single layer of H₂S molecules which had been adsorbed during the preparation. If the rate of evaporation were very small the surface would be practically completely covered and the rate of reaction with phosphate would

¹ Cf. Rideal: Trans Faraday Soc., 19, 90 (1923-24).

be independent of the phosphate concentration and of zero order. This explanation seems less probable than (a) as it must also be assumed that H_2S is transferred to the underlying layer of uncombined PbS as the reaction proceeds. The poison could not be HS' since, given the usual magnitude of the electric charge on a particle, the ions could only be relatively sparsely distributed on the surface.

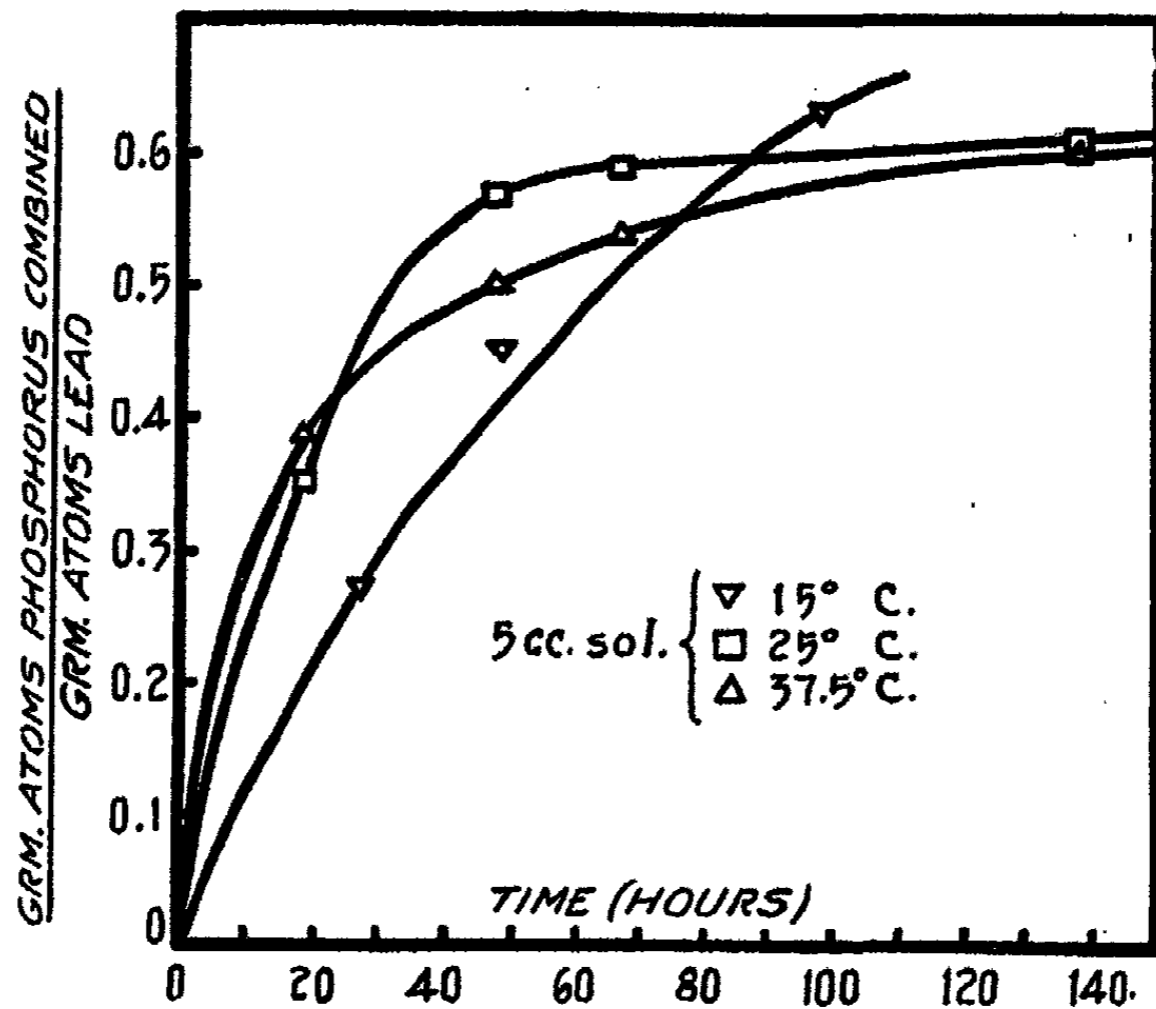


FIG. 3

Similar experiments were carried out at 25° and 37.5° C. The amount of sedimentation was greater than at 15° C; at 37.5° the particles had settled out almost completely after 70 hours.

The results are given in Tables IV and V.

TABLE IV

$t = 25^\circ C$
 100 cc. 0.0018 M. phosphate solution.

| Time (hours) | 5.0 cc. PbS sol. P/Pb | 10 cc. PbS sol. P/Pb |
|--------------|--------------------------|-------------------------|
| 18 | 0.35 | 0.22 |
| 47 | 0.57 | 0.41 |
| 67 | 0.59 | 0.49 |
| 138 | 0.61 | 0.60 |
| 306 | 0.62 | 0.62 |
| 474 | 0.62 | 0.64 |

TABLE V

$t = 37.5^\circ \text{C}$
100 cc. 0.0018 M. phosphate solution.

| Time (hours) | 5.0 cc. PbS sol. P/Pb | 10 cc. PbS sol. P/Pb |
|--------------|--------------------------|-------------------------|
| 18 | 0.39 | 0.30 |
| 47 | 0.50 | 0.40 |
| 67 | 0.54 | 0.46 |
| 138 | 0.60 | 0.57 |
| 306 | 0.62 | 0.63 |
| 474 | 0.62 | 0.64 |

Values of k calculated from these results decreased with time, the decrease being greater at 27.5° . The results with 5 cc. sol for the three temperatures are plotted in Fig. 3.¹ It will be seen that while the initial rate of combination increases with temperature the reverse is the case towards the end of the reaction. The decrease in rate corresponds with the observed increased rate of particle aggregation. It appears therefore that aggregation of the particles causes a decrease in the reacting surface. This is supported by experiments at 25° and 37.5° where the sol was added to a phosphate solution containing 0.5 per cent gelatin. There was then practically no sedimentation of the particles. The quantitative results were irregular (the passage of small amounts of gelatin through the ultra filter interfered with the subsequent estimation of phosphate) but together with the rate of colour change they showed that the reaction was faster throughout at 37.5° .²

The aggregation of the particles must be attributed to at least a partial removal of the protective coating of gelatin on dilution with the phosphate solution followed by a slow flocculation by the electrolytes present. The falling off in the rate of reaction when the amount of colloid present was increased indicates that the rate of aggregation, in addition to being a function of the temperature, is also a function of the concentration of colloid particles.³

Summary

1. A method for the preparation of a lead sulphide sol is described using gelatin as a protective agent.
2. The percentage transformation of lead acetate into colloidal lead sulphide is dependent on the initial concentration of lead acetate. This is attributed to a decrease in the velocity of nuclei formation in concentrated acetate solutions whilst the velocity of growth of the nuclei remains unaltered.

¹ It was found that the rate of combination at 25°C was independent of the phosphate concentration.

² It was possible to obtain a rough value for the critical increment of the reaction from these results, namely of the order of 15,000 calories.

³ Paine: Proc. Cambridge Phil. Soc., 16, 430 (1910-12) found that in the slow flocculation of a CuO sol by electrolytes the rate was directly proportional to the square of the initial concentration of colloid.

3. The rate of combination of lead sulphide particles with phosphate ions has been measured. The rate is slow compared with the rate of diffusion of phosphate ions to the surface and is independent of the phosphate concentration over the range investigated.

4. The results at 15°C are in agreement with a rate of reaction proportional to the surface of unchanged particle. At higher temperatures aggregation of the particles causes a decrease in reacting surface in addition to the decrease due to combination. A probable explanation of the zero order of the reaction is that combination takes place between the surface and adsorbed phosphate ions, the number of adsorbed ions per unit area being independent of the phosphate concentration over a wide range.

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May 23, 1928.*

EVOLUTION OF THE ODD-NUMBERED ELEMENTS

BY W. V. HOWARD

Introduction

A reading of Aston's "Isotopes" and various papers by Harkins,¹ and Clarke led the writer to endeavor to predict the isotopes of those elements which had not yet been examined, and also to try to find out whether or not there was some sort of serial arrangement which might possibly indicate a process of evolution. Accordingly, he plotted the isotopes of the even-numbered elements which had been reported in Aston's book and found that there seemed to be definite series of elements whose mass numbers differed by four, and whose atomic numbers differed by two. That is, there were series whose mass numbers could be expressed by one or other of the following formulae:²—

$$M = 2N + 4X \quad \text{or} \quad M = 2N + 4X + 2,$$

where M is the atomic weight, N is the atomic number and X is an integer between 0 and 13. (See Fig. 1.) In the original graph, the relationships between the radioactive elements differed from those between the non-radio-active elements, so they were omitted. Also, the elements below carbon were omitted because the relationships between these seemed to be different from those in the elements occurring above carbon.

Isotopes of Odd-Numbered Elements

In dealing with the odd-numbered elements, it was found that the same serial arrangement prevailed, but the surprising fact was, that, with very few exceptions, every even-numbered element was preceded by an odd-numbered element whose isotopes had mass-numbers which were less by one than one or the other or both of the two lowest isotopes of the even-numbered element. (See Fig. 2).

Odd Mass Numbers in Isotopes of Even-Numbered Elements

Although no odd-numbered element (above oxygen and below lead) has an even mass-number, several even-numbered elements have odd-numbered isotopes. These include zinc, selenium, krypton, tin, xenon and mercury. Of these zinc, krypton and mercury definitely end one or two series whose members satisfy the formulae referred to above for a given value of X and it is probable that xenon does also. Also there is some irregularity in connection with the odd-numbered elements preceding krypton and xenon, and therefore selenium and tin may also end series.

¹ Chiefly W. D. Harkins: "The Evolution of the Elements", J. Am. Chem. Soc., 39, 864 (1917) and F. W. Clarke: "The Evolution and Disintegration of Matter", U. S. Geol. Survey, Prof. Paper 132-D (1924).

² The values $4X$ and $4X + 2$ are the same as the isotopic numbers of Harkins: Phil. Mag., (6) 42, 305-339 (1921).

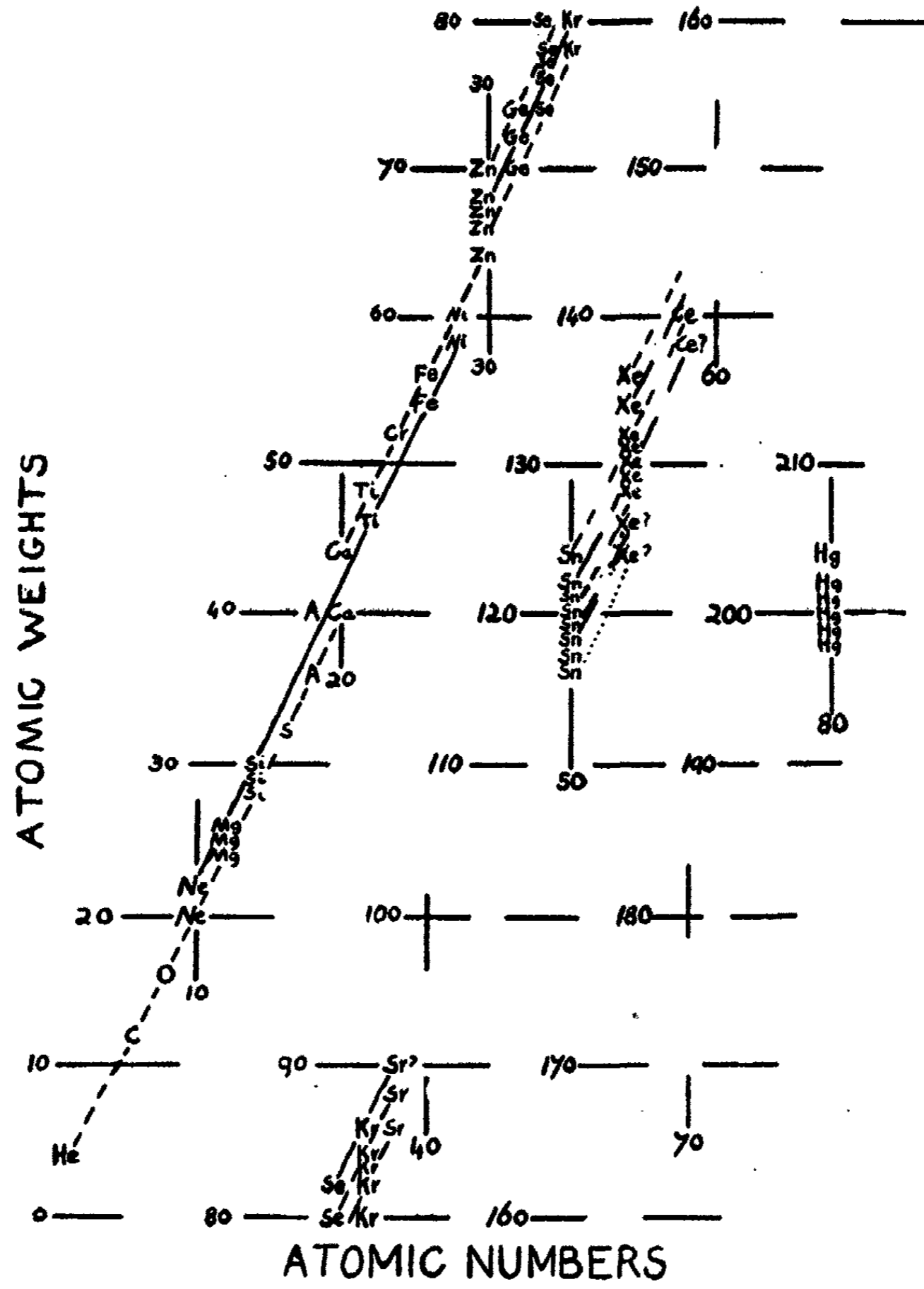


FIG. 1
Isotopes of even-numbered elements as reported by Aston

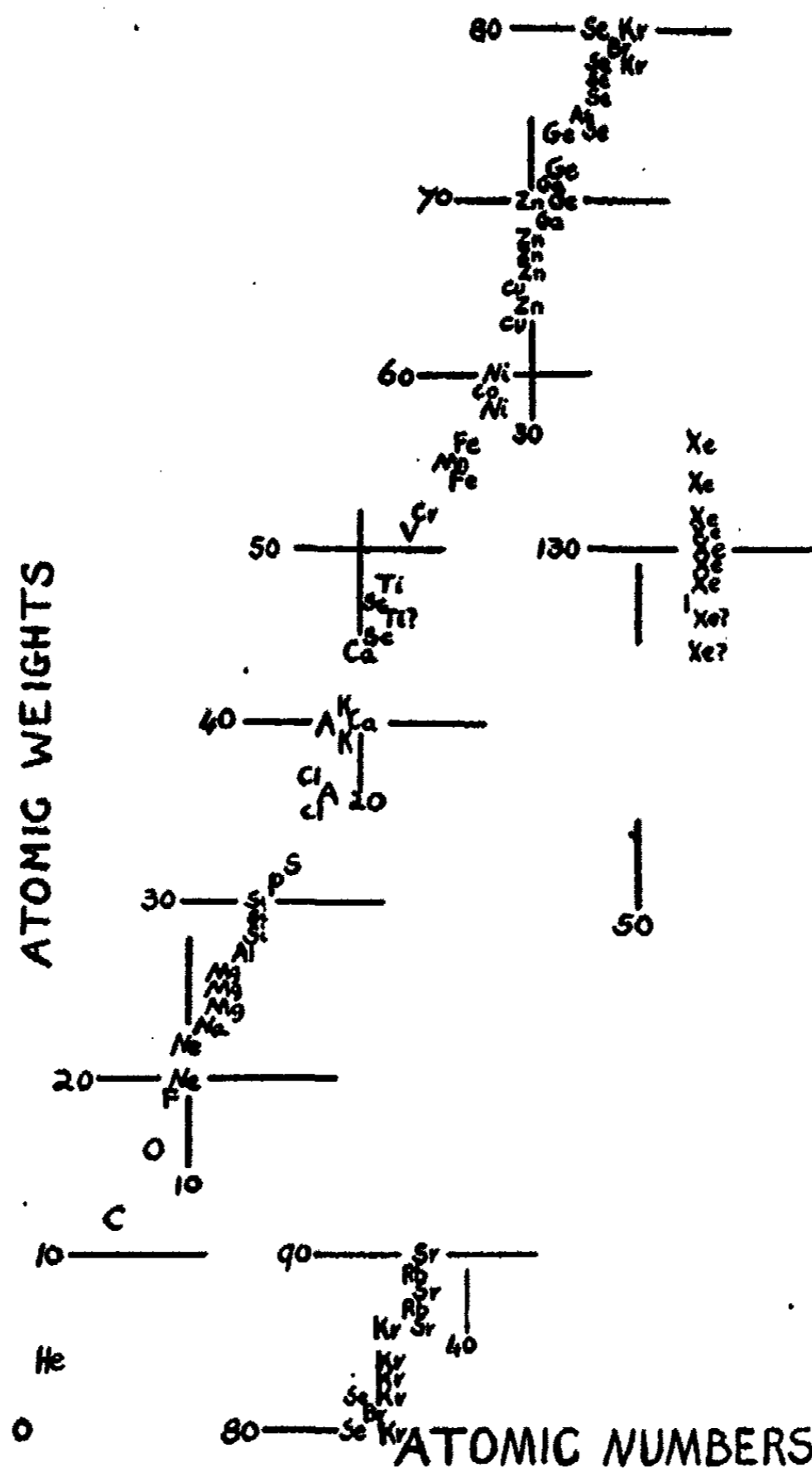


FIG. 2
Isotopes of elements reported by Aston

Relations between Elements

The following rules may be formulated for the elements between carbon and polonium (except nitrogen).¹

(a) The isotopes of the even-numbered elements form two groups of series of which one group conforms to the equation

$$M = 2N + 4X$$

and the other to the equation

$$M = 2N + 4X + 2,$$

where M is the mass number of the isotope, N the atomic number of the element and X any whole number between 0 and 11, or between 0 and 13 if the radio-active elements are included.

(b) Each series corresponding to any given value of X in one or other of the two equations is terminated by an element which has an odd-numbered isotope, and in some cases two odd-numbered isotopes.

(c) The odd-numbered isotopes of the even-numbered elements may lie immediately above the lowest and second lowest even-numbered isotopes, or above either of these, but do not occupy a higher position in the list of isotopes of any element.²

(d) The elements whose lower isotopes terminate one or two series have higher isotopes which begin one or two others. As an obvious corollary it may be stated that the even-numbered elements which contain odd isotopes have a larger number of even isotopes than neighboring even numbered elements which have no odd isotopes.

(e) Few elements have more than five even-numbered isotopes.

(f) The above rules do not hold in their entirety for the two series in which $X = 0$.

(g) No odd-numbered element has more than two isotopes.

(h) No odd-numbered element has an isotope with an even mass number.

(i) No odd-numbered element has an isotope whose mass number is the same as that of any isotope of any other element, odd or even.

(j) If an odd-numbered element has two isotopes, the following even-numbered element cannot have more than one odd isotope.

(k) The isotopes of all odd-numbered elements have a mass number which is less by one than one or other or both of the two lowest isotopes of the even-numbered element immediately following.

If the isotopic numbers of Harkins are used in place of the values $4X$ and $4X + 2$ it will be found that most of the rules as stated above have been anticipated by Harkins. The isotopes predicted by Harkins³ vary radically from those of the writer owing to the fact that the relations noted in rule (k) have not been stated by Harkins.

In several cases certain elements are believed to end series, and will thus have odd isotopes, in spite of the fact that the following even-numbered ele-

¹ Russell's rules are the same as these in many respects (*Nature*, 112, 588 (1923)).

² This, of course, cannot apply to the radioactive elements.

³ *J. Franklin Inst.*, 195, 551-573 (1923).

ments have isotopes in the same series. These latter elements which include krypton, xenon, and tin do not follow the rule regarding the distribution of odd isotopes. Thus the odd isotope of krypton is found above the third even isotope rather than the second, xenon has two even isotopes followed by alternating even and odd, and tin has no fewer than four odd isotopes which are placed above the second, third, fourth and fifth even isotopes. In these cases, it is believed that the preceding elements do not present the same degree of instability as do the elements which ordinarily terminate series.

These apparent exceptions to the rules given above, indicate the possibility that further examination may disclose the presence of still others. This will necessitate a modification of the rules, but will not affect the relations existing between the odd numbered elements and the following even numbered elements, except insofar as the position of the related isotopes is concerned.

In the cases of krypton, xenon and tin, the preceding odd-numbered elements have positions which are not in accord with rule (k) bromine is related to the second and third isotopes of krypton, iodine to the third isotope of xenon and, from its atomic weight, indium is believed to be related to the third lowest isotopes of tin, in spite of the fact that Aston has found an isotope of tin which has the same mass number.

Chlorine has two isotopes Cl 35 and Cl 37. There is a corresponding isotope of argon A 36, but no A 38, nor is there a Ca 43 following K 41. In the case of argon, it may be stated that the inert gases appear to present exceptions to many of these rules—vide krypton and xenon above.

Prediction of Unknown Isotopes

It was found that these rules were not sufficient to permit the prediction of the isotopes of the other elements, chiefly because no rule could be formulated which would indicate which elements should terminate series. Certain series in the group $M = 2N + 4X$ were terminated as follows:— Series 0 (i.e. $X = 0$) is terminated by calcium, series 1 by zinc, series 2 by krypton, series 3 by cadmium, series 4 by tin and series 5 by xenon, and it is probable that series 10 is terminated by polonium, but the position of the elements terminating series 6, 7, 8, and 9 can not be determined as most of them fall within the rare earth group. Similarly in the $M = 2N + 4X + 2$ group, series 0 is terminated by nickel, series 1 by selenium, 3 by cadmium and 9 by mercury. Series 4 is believed to be terminated by tellurium by analogy with selenium. Also by analogy with nickel, it is possible to assume that series 2 is terminated by ruthenium and series 8 by osmium. Polonium is believed to terminate series 10, leaving series 5, 6, and 7 to end somewhere within the rare earth group.

A. S. Russell has endeavoured to predict the mass numbers of the isotopes of the elements² and the writer's efforts resulted in such close agreement with his that an attempt was made to try to fit Russell's results to the rules already formulated. According to Russell, the following ele-

² A. S. Russell: *Phil. Mag.*, 47, 1121-1140; 48, 365-378 (1924).

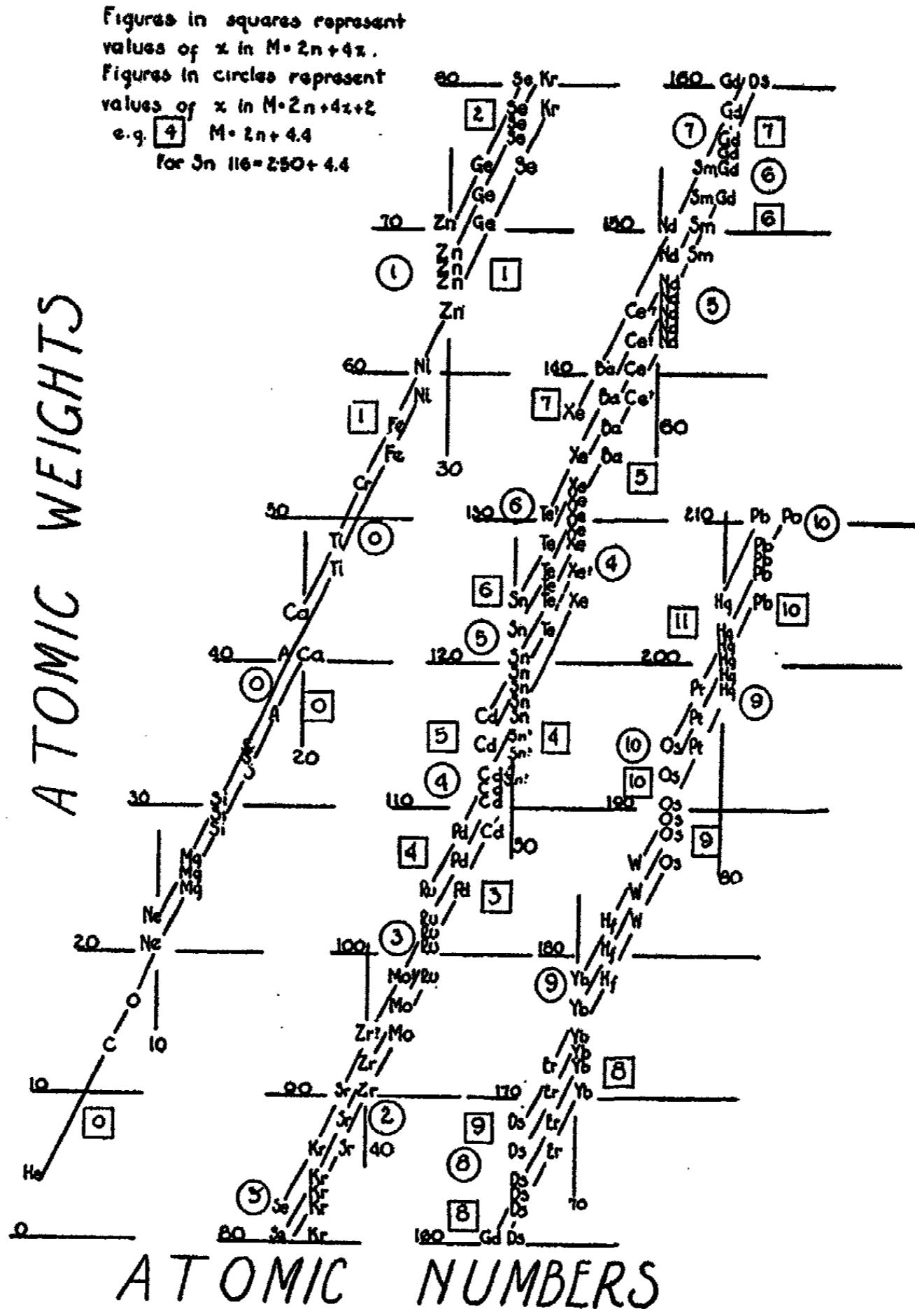


FIG. 3
 Even-numbered elements
 Isotopes of even-numbered elements between Carbon and Polonium

ments lying between xenon and mercury have at least one odd isotope, neodymium, gadolinium, dysprosium, ytterbium, hafnium and osmium. Using the mass numbers given by Russell for the isotopes of these elements, it is possible to show that all except hafnium both end and begin series so that

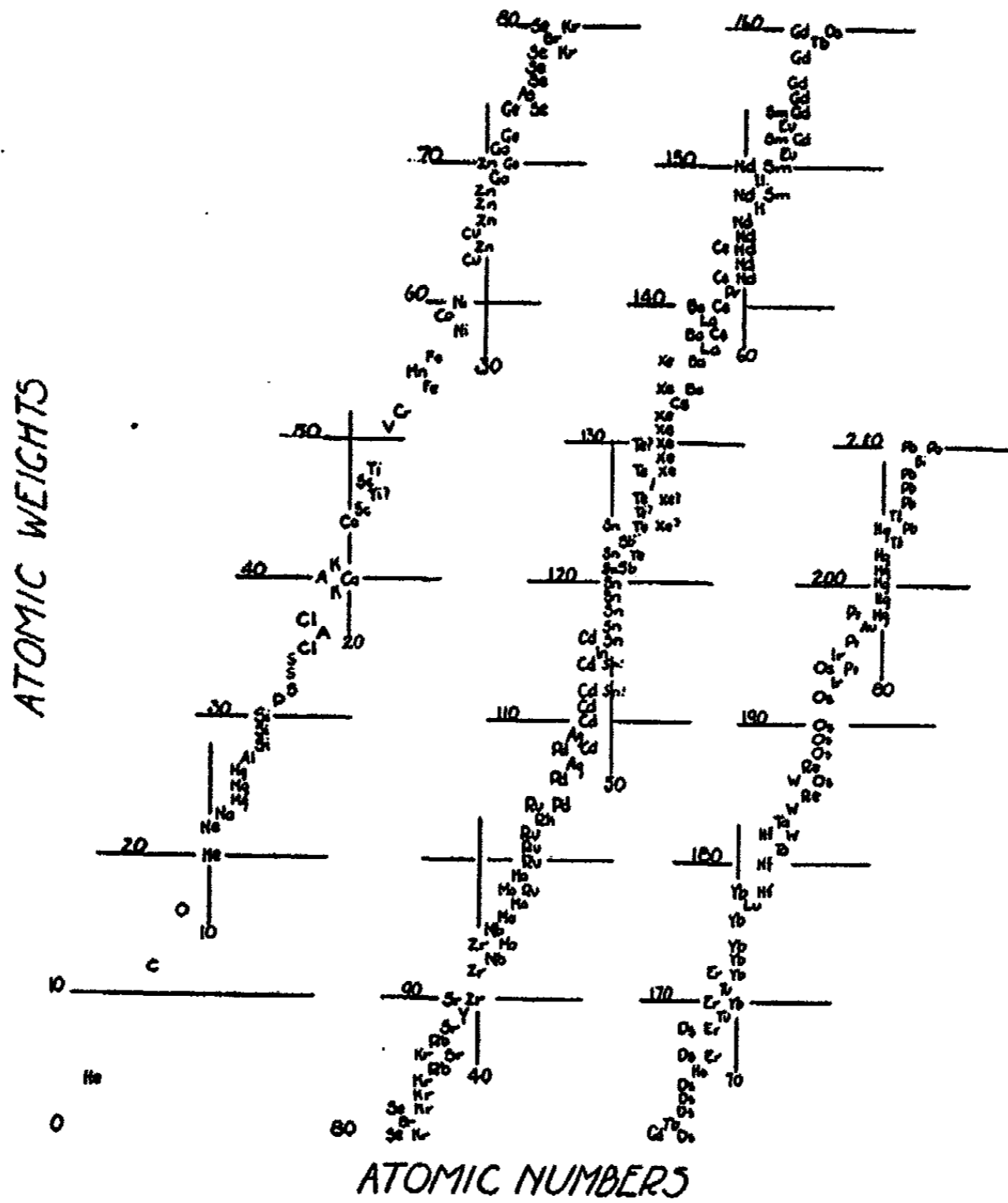


FIG. 4
Odd and even-numbered elements
Isotopes of all non-radioactive elements above carbon

the difficulty presented by the rare earth group is solved; except for the value Hf 179. With these additional data the completed tables were prepared. (Figs. 3 and 4.)

These tables differ from the results of Aston in very few cases, as an attempt was made to begin with Aston's results and to reason from them. In some cases questionable values found by Aston were omitted. Thus Ti

50 is not believed to exist, for if it does then we should expect that there would be an odd-numbered isotope of titanium and also one with a value Ti 44. (See rule (d) above.) On the other hand, the experimentally doubtful Zn 67 is believed to exist since zinc follows this rule (d) in other respects. Aston found no value Sr 90, but it is believed that this exists in order to maintain the continuity of the series $M = 2N + 4X + 2$ ($X = 3$) which begins with Se 86 and ends with Cd 110.

Owing to the different methods used in calculation by the writer and by Russell, there is a little more disagreement between our results. Some of Russell's values (such as Mn 53, Co 57) do not agree with experimental results and are therefore omitted from the tables. With the exception of the value Hf 179 none of the other points of disagreement are of great importance. Most of them are due to the fact that the writer has considered that the series are continuous and he has been forced to add one or more isotopes to some elements. These, if present at all, are not abundant. If, however, Hf 179 exists, then by rule (d) hafnium must end a series. If it does, then Hf 176 must also exist. If it ends a series, then by the same rule, it must begin one. If it begins one, the values Hf 184 and W 188 are necessary. In other words the writer is either forced to disagree once with Russell and omit the value Hf 179, or to add three other values which Russell does not admit, and which are, indeed, unnecessary so far as the writer's hypothesis is concerned.

Evolution of the Elements

The first elements to form were the even-numbered elements between carbon and nickel, together with hydrogen and helium. These last elements appear to be the material from which all elements are derived, although the above outline of the relations between the elements does not indicate the precise manner in which the more complex elements were built up. Between carbon and calcium the elements have mass-numbers which either equal twice the atomic number or are equal to twice the atomic number plus two (i.e. $X = 0$). In the latter series there are many gaps, thus there is no representative in this series of carbon, oxygen, argon, or calcium. It would appear, then, that the isotopes of the elements which belong in the $M = 2N + 4X + 2$ series ($X = 0$) developed from the lower isotopes which lie in the $M = 2N + 4X$ series ($X = 0$). The atomic weights of the elements which lie between carbon and chromium show that the most abundant isotope of those elements which have more than one isotope is the one lying in the $M = 2N + 4X$ series. Thus the atomic weight of neon is 20.2 (isotopes 20 and 22), that of magnesium is 24.32 (isotopes 24, 25, and 26) of silicon 28.07 (isotopes 28, 29, and 30.)

The statement that evolution began with the formation of the even-numbered elements from carbon to nickel, with hydrogen and helium is based on our knowledge of the meteorites and the deductions that have been made from this knowledge as regards the earth. Astrophysics provides much confirmatory evidence. As later evolution followed a somewhat dif-

ferent course although the same general principles were involved, it is to be expected that the elements below nickel would have different characteristics from those above. Thus the series are not continuous below nickel, and unstable conditions seem to have caused magnesium, silicon, and sulphur to form an odd-numbered isotope.

Following the formation of these elements, the evolutionary processes continued in three ways, namely, the formation of the higher even-numbered elements, the odd-numbered elements and the elements between nitrogen and lithium.

The even-numbered elements whose mass numbers are higher than those of nickel may have been formed by the addition of either helium atoms or of neutrons to atoms already formed. When helium atoms are added, the properties of the atom are changed and a new element is formed. The new element, however, is a member of the same series as the old. Thus in the series $M = 2N + 4X$ ($X = 2$), ${}_{30}\text{Zn } 68$ is the first member. On the addition of a helium atom ${}_{32}\text{Ge } 72$ is formed; then ${}_{34}\text{Se } 76$ and finally ${}_{36}\text{Kr } 80$.

The addition of helium atoms cannot continue indefinitely and as the atomic weight increases the elements become unstable unless more than two negative charges are added to the nucleus for every four protons. In such a case neutrons are added, usually in pairs. If, however, the degree of instability possessed by end-members of a series is reached, neutrons may be added singly although this addition of single neutrons will not continue after the formation of the third even isotope, because of the increasing stability of the atom. The elements whose lower isotopes and series require the addition of a larger number of neutrons than do the others for precisely the same reason that they end series; namely because they are more unstable than those elements which immediately precede them in the periodic table. They therefore add enough neutrons to enable them to begin new series.

From this it can be seen that the lower isotopes of any element will be less stable than the higher ones. It may, therefore, be expected that the lowest isotopes are present in less abundance than the second lowest, which, in turn, will not be as abundant as the third lowest. The higher isotopes, on the other hand, are formed as a result of the instability of the lower ones and the quantity so formed may be very small.

The odd-numbered elements were formed by a process of disintegration of the even-numbered elements, whereby one or both of the two lowest (and therefore the least stable) isotopes lost one positive charge from the nucleus and one electron. This proton and electron formed a hydrogen atom which may have gone into the formation of higher isotopes of even-numbered elements or may have remained as a hydrogen atom which later became a hydrogen molecule. Since the valence of the odd-numbered elements is less than that of the even-numbered elements immediately following, it follows that for every two atoms of an odd-numbered element formed two atoms of hydrogen and one of oxygen are given off.

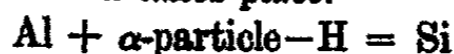
Applying these principles of evolution and disintegration to the elements below carbon, a scheme may be outlined which can account for their irregularities but this scheme is hardly more than a guess, probably a very poor

one, at that. If it be assumed that nitrogen was formed in the ordinary way by some such combination as three helium and two hydrogen atoms, and then, by a process of disintegration, it lost first one helium atom and then another, ${}^5\text{B}_{10}$ and ${}^3\text{Li}_6$ could be formed. Also ${}^5\text{B}_{11}$ could be formed by the loss of one proton and one electron from carbon, and this would give off one helium atom forming ${}^3\text{Li}_7$. ${}^4\text{Be}_9$ is formed from ${}^5\text{B}_{10}$ by the loss of one proton and one electron. Thus the elements below nitrogen reverse the usual plan, and the odd-numbered elements act in the same way as do the even-numbered elements above nitrogen and vice-versa.

So far the hypothesis has been stated with as little detail as possible so as to present its major features. Naturally, since it deals with the very fundamental processes of chemical and geological change it is necessary to inquire further into it in order that we may see whether or not it will fit observed facts and furthermore whether or not it will solve existing difficulties. Until it can be shown that the hypothesis can be applied it would seem of little avail to consider further a revolutionary idea that is based solely on certain numerical relations and predictions based on these relations.

Experimental Evidence

Rutherford and Chadwick bombarded certain elements of low atomic number with α -particles and obtained hydrogen. As a result of these experiments, it was found that the hydrogen atoms driven off from elements of even atomic number had a shorter range than those driven off from elements of odd atomic number indicating that the even-numbered elements were more stable than the odd, insofar as this particular bombardment was concerned. This did not, however, indicate anything else, in the writer's opinion, as regards the stability of the atoms except that they differed from one another. The process, if it exists, whereby odd-numbered elements are formed from even, is not a bombardment of the elements within the crust by alpha-particles but a natural disintegration which is analogous to radioactive disintegration though quite different from it in detail. Perrin¹ suggests that the following reaction takes place.



This equation in terms of atomic weights may be expressed:

$$27 + 4 - 1 = 30.$$

and in terms of atomic numbers

$$13 + 2 - 1 = 14.$$

If, however this process is applied to such an element as manganese, we have the following results:

$$\text{Atomic weights:— } 55 + 4 - 1 = 58 \text{ (nickel)}$$

$$\text{Atomic numbers:— } 25 + 2 - 1 = 26 \text{ (iron)}$$

In other words, if an odd-numbered element is not followed by an even-numbered element with an isotope having a mass-number which is greater by three than that of the odd-numbered element, this reaction can not take place in this way.

¹ Quoted by Rutherford: *Nature*, 115, 493 (1925).

Gold derived from Mercury

The derivation of gold from mercury which was reported by Miethe¹ and later by Nagaoka² has a considerable bearing on this hypothesis. Although later tests, using Miethe's methods, failed to achieve positive results, the writer is informed by Dr. A. L. Day³ that Nagaoka's work has been re-submitted to careful scrutiny and that tests on mercury previously purified by an independent investigator of his process gave a positive result.

The suggestion of Stumpf⁴ that the isotope of mercury 197 originally reported by Aston⁵ was really gold is of interest. The fact that extremely careful refinement is necessary to remove all traces of gold from mercury would tend to indicate some process whereby gold was actually being formed from mercury, and the fact that mercury which has been refined with especial care shows no trace of gold might indicate that the process of disintegration is very slow. The writer would be very much interested in seeing the results of experiments in which mercury, refined to such a degree that it contained no trace of gold, was allowed to stand for a year or more before being retested in order to see whether or not gold could be obtained.

In case this transmutation actually takes place it is probably the isotope of mercury 198 which breaks down to form gold 197. In that event, if enough gold were found to make any appreciable effect upon the mercury, it would be interesting to find out whether or not the atomic weight of the mercury had actually increased and also whether or not the isotope 198 was less abundant than before the disintegration was effected. The successful performance of this experiment would indicate to some extent the correctness of the writer's hypothesis, as it is to be expected that elements of higher atomic weight would give better results than those of lower atomic weight. The formation of gold from mercury would be more easily demonstrated than any other such change except possibly the formation of thallium from lead.

Piutti and Boggio-Lera⁶ are reported by Nature⁷ as stating that the view that mercury may undergo spontaneous transmutation into gold is suggested by the invariable presence of gold in commercial mercury. The transmutation of lead to mercury and thallium was reported by A. Smits⁸ and in endeavoring to explain both the transmutation of mercury to gold and of lead to thallium, Davies and Horton⁹ point out that "the change might conceivably be effected either by the entry of an electron into, or by the removal of a proton from, the nucleus of the mercury atom. The same alternatives present themselves in regard to the transformation of lead (82) into thallium (81)"

¹ Nature, 114, 197 (1924).

² Nature, 116, 95 (1925).

³ Personal communication.

⁴ Nature, 115, 172 (1925).

⁵ "Isotopes" (1924). Later determinations have shown that Hg 197 does not exist.

⁶ Rend. Accad. Sci. Fis. Matem. (Naples) Sept-Dec. (1925).

⁷ 117, 604 (1926).

⁸ Nature, 117, 13 (1926).

⁹ Nature, 117, 152 (1926).

In this connection it might be pointed out that the transmutation of elements below lead cannot be due to radioactive processes, and mercury 198 and gold 197 cannot simply be lower members of the radioactive series. It is true that Hg 204 might be formed as a result of the radioactive disintegration of thorium lead, but from this point disintegration would have to proceed from one isotope of mercury to another, something that might conceivably happen if the higher isotopes were derived from the lower, and then follow a third method whereby Au 197 could be formed. Thus there would be two new modes of disintegration besides the two radioactive methods which would seem entirely unlikely, and it would seem impossible to derive gold from lead by any single process.

The Composition of Meteorites, etc.

The great preponderance of even-numbered elements over odd-numbered elements in the meteorites has already been pointed out by Harkins¹ and others. This was regarded by Harkins as evidence of the greater stability of the even-numbered elements, but it would seem more probable that it is evidence that, normally, only the even-numbered elements would form and that the odd-numbered elements are formed at a later time.

Harkins, in the same articles, pointed out that wherever an odd-numbered element was at all abundant, the neighboring even-numbered elements were still more abundant. This might be believed to be indicative of the disintegration of the latter to form the former, especially if the relation between the odd-numbered elements and the lowest isotopes of the even-numbered elements be considered.

The only odd-numbered elements found in any abundance in the iron meteorites are cobalt and phosphorus and both nickel and sulphur are also present, although sulphur is not so abundant as phosphorus. In many meteoric irons a considerable amount of hydrogen has been found which substantiates the idea that the cobalt may have been formed by the disintegration of nickel with the formation of hydrogen.

In the meteoric stones, cobalt, aluminum, sodium, potassium, and phosphorus are all present, but in no case in the average composition does any one of these elements occur in quantities greater than 10% of the even numbered elements immediately following.

In the achondritic meteorites, the same odd-numbered elements are present with manganese in addition, and here too, none of them are more than one-tenth as abundant as the even-numbered elements immediately following with the exception of aluminum which amounts to less than one-seventh of the silicon present.

In Clarke's paper on the evolution and disintegration of matter² he points out that the Class B stars contain besides helium and hydrogen, silicon, oxygen and nitrogen, and that in the class A stars magnesium, calcium, iron and titanium are beginning to appear. With the exception of nitrogen, these

¹ Harkins: *J. Am. Chem. Soc.*, 39, 877 (1917); *Phil. Mag.* (6), 42, 305-339 (1921).

² U. S. Geol. Survey, Prof. Paper, 132 D (1924).

elements together with carbon, chromium and nickel, all of which are found in the meteoric irons, make up the two series in which $X = 0$ and seem to be the elements from which all others are derived. Nitrogen has been referred to as the possible source of the lightest elements, except helium and hydrogen. The two additional members of the 0 series, argon and neon, do not appear to fit into the general scheme¹ unless, being gases at normal temperatures, they were too volatile when formed to be retained by the parent mass and were dissipated into space.

The relative abundance of elements in the Sun's atmosphere is given by Washington² as follows: calcium, iron, hydrogen, sodium, nickel, magnesium, cobalt, silicon, aluminum, titanium, chromium, strontium, manganese, vanadium, barium, carbon. Of the odd-numbered elements in this list, exclusive of hydrogen, sodium is more abundant than magnesium, but all of the others are less abundant than their possible source-elements. Aluminum is very close to silicon and this gives rise to the suggestion that sodium is the easiest of all the odd-numbered elements to form, with aluminum next. As a matter of fact, potassium is also abundant in the sun's atmosphere of which it forms, together with hydrogen, the outer layer. Thus, in the sun's atmosphere, the most abundant odd-numbered elements are identical with the most abundant odd-numbered elements on the earth's crust and, in addition, the hydrogen formed as a result of the disintegration of the even-numbered elements is also present in great abundance. This would seem to be more than a mere coincidence.

Association of Elements within the Earth

In a few cases odd-numbered elements are found associated with the even-numbered elements from which they are believed to be derived. Examples of this association include copper and zinc, and cobalt and nickel in ore deposits, and silicon and aluminum in igneous rocks. Other associations are, however, equally common. These include sodium and iron, sodium and calcium, and potassium and magnesium in igneous rocks, and lead and silver, lead and zinc, and gold and silver in ore deposits. The latter group of associations are undoubtedly due to processes of differentiation which have resulted in the concentration of these elements in a certain portion of the magma which contained them and there is no reason why the first group should not have become associated as a result of the same causes without any reference to their original relationship.

In their chemical properties the odd-numbered elements tend to be more like the even-numbered elements that follow them than those which precede them. Among other well known examples of this similarity are vanadium and chromium, manganese and iron, cobalt and nickel, copper and zinc. It is possible that this chemical relationship may indicate a genetic relationship as well.

¹ See W. D. Harkins: *Phil. Mag.*, (6) 42, 321 (1921).

² H. S. Washington: *Am. J. Sci.*, 9, 376 (1925).

The Hypothesis of Atomic Disintegration and the Planetesimal Hypothesis

The planetesimal hypothesis may be summarized as follows in so far as it affects the formation of the earth:

1. Slow accumulation of planetesimal matter.
2. Accumulation of atmosphere after the planet had attained a sufficient size to hold it. Additional solid planetesimals were added, however, afterwards so that some of the gases became occluded in the rocks and have been coming to the surface since the beginning of geologic time.
3. Self compression due to gravity gave rise to sufficient internal heat to cause liquefaction of rocks at certain places thus promoting volcanic activity.
4. Water vapor in the atmosphere condensed and formed the hydrosphere to which, like the atmosphere, large additions have been made by vulcanism.

The chief objection to this theory in the writer's opinion lies in the idea of an initial volcanic stage caused by compression. If compression gave rise to the initial vulcanism, then a different cause must be assigned to later vulcanism. The authors of the Planetesimal hypothesis tacitly assume that pre-Cambrian vulcanism, especially Archean vulcanism, was more intense than more recent vulcanism and that therefore pre-Archean vulcanism was probably still more intense. Is it not more reasonable to assume that, except for minor variations, vulcanism is fairly uniform but that Archean vulcanism seems more widespread because of the greater duration of the Archean than, say, the Cenozoic, and also the fact that much of the sedimentary record of the Archean is lost?

Barrell's hot-earth theory is even more difficult to understand. The idea of a globe so heated by great masses of planetesimal matter which come charging into it becomes almost untenable in the light of the evidence which is accumulating to the effect that the earth is composed of more or less uniform shells which grade into one another. These shells could not have formed unless there was a slow accumulation of matter in a relatively fine state which was added to the central core in inverse order of its specific gravity. Accumulation was probably slow. In fact, considering the small size of the particles, it is quite possible that all heat of impact and heat of compression was dissipated before the earth had reached its present size.

At this point, the theory of radioactive control of mountain-building becomes involved.¹ According to this theory vulcanism and mountain-building are caused by evolution of heat due to the disintegration of the uranium and thorium series. The chief difficulty in this hypothesis lies in the quantities involved. For example Holmes² in 1915 shows that with a cooling earth the fact that there is a gradually diminishing amount of radioactive material with depth helps the theory since volcanic temperatures can be more satisfactorily obtained by an earth cooling down from 1000° with its rate of cooling retarded by radioactivity than by heating by radioactivity alone.

¹ J. Joly: "Surface History of the Earth" (1925) and earlier papers by Holmes, Joly et al.

² A. Holmes: "Radioactivity and the Earth's Thermal History", *Geol. Mag.*, 52, 112 (1915).

Later Holmes¹ decided that "there must be more uranium and thorium in the deep-seated rocks than has hitherto been thought possible" because of the necessity of abandoning the theory of a cooling earth.

T. C. Chamberlin² pointed out, as early as 1906 what seems to be the fundamental objection to the radioactive control theory, namely that since radioactivity generates heat sufficient to raise the temperature of rocks to the melting point, the rocks immediately surrounding the radioactive materials must melt and the radioactive materials must therefore be transferred to the surface. The quantity of radioactive material in the earth's crust must diminish with depth.

Anticipating later arguments, it may be pointed out that the formation of the odd-numbered elements from the even must be accompanied by the evolution of heat. Paraphrasing Chamberlin's argument, the material in the immediate vicinity of this reaction melts and the odd-numbered elements are transferred to the surface. They are continually being transferred to the surface and since the process of atomic disintegration may be considered as being continuous, there seems to be no reason for assuming the existence of any initial volcanic stage which differed radically in intensity from any later volcanic stage.

Introducing this idea into the statement of the planetesimal hypothesis as outlined above, we have:—

1. Slow accumulation of planetesimal matter.
2. Disintegration of even-numbered elements to form odd-numbered elements and hydrogen. The hydrogen combined with oxygen to form water which, together with other gases and the melted rocks, rose towards the surface causing volcanic activity.
3. The water and other gases brought to the surface as a result of vulcanism gave rise to the hydrosphere and atmosphere.

Since the hypothesis of atomic disintegration outlined in the foregoing pages has been called on in order to present this modified form of the planetesimal hypothesis, it is necessary to consider several additional points.

Is the quantity of heat liberated sufficiently great to account for the following, (1) the rise in temperature from a cool globe to one with a thermal gradient such as that of the earth at present, (2) the latent heat of fusion of the igneous rocks of the earth's crust, (3) the quantity of heat radiated from the earth since the beginning of geological time, (4) the heat absorbed during the process of formation of the complex elements?

Would the reaction be periodic so that recurrent periods of mountain building and volcanic activity could take place followed by periods of comparative quiet?

What effect would differentiation have on magmas formed according to this hypothesis?

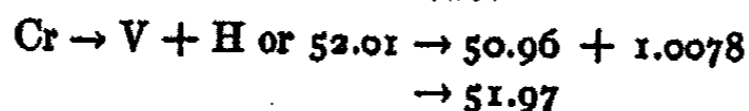
¹ A. Holmes: *Geol. Mag.*, 62, 514 (1925).

² "Origin of the Earth" (1906).

Heat involved in Disintegration

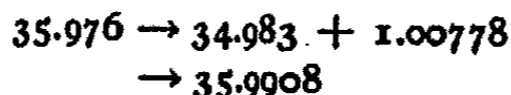
In considering the quantity of heat involved in the process of atomic disintegration, there are several sources of heat as well as several reactions which would tend to absorb heat. Of these, the most important are the disintegration of the even-numbered elements to form odd-numbered elements and atomic hydrogen, the heat of formation of molecular hydrogen, the heat of formation of water, the heat of formation of the elements of higher atomic weight than nickel, and the heat of formation of helium from hydrogen.

In calculating the amount of heat generated or absorbed by the disintegration of the even-numbered elements it is necessary to ascertain whether or not there has been a loss in mass or a gain in mass during the disintegration. Since most of the elements have one or more isotopes, it is difficult to determine whether or not there has been any loss in mass. In fact the only even-numbered element that is believed to be a simple element which is preceded by an odd-numbered element having the normal relationships to it, is chromium. Here the reaction is as follows:—



involving a loss in mass of 0.04 g. per gram of hydrogen formed.

If, on the other hand, Aston's latest determinations of mass numbers¹ are correct, there would be a gain in mass if odd-numbered elements and hydrogen are derived from even-numbered elements. Thus if $\text{A} \rightarrow \text{Cl} + \text{H}$



or a gain in mass of 0.014 g. per gram of hydrogen formed.

Rutherford states that the energy liberated in the formation of 1g. He from H would be 1.6×10^{11} cal.² so that if 4 grams of helium were formed 6.4×10^{11} cal. would be liberated and there would be a loss in mass of 0.0311 g. if the atomic weight of helium is 4.00 or if Aston's determination of the atomic weight is correct, a loss of 0.02896 g. That is, either 2×10^{18} or 2.2×10^{18} cal. are liberated for every gram loss in mass.

There are therefore two possibilities. In the first case, there is a loss of mass of between 0.03 and 0.04 g. for every gram of hydrogen produced which would amount to 0.9×10^{23} g. or 1.2×10^{23} g. for the hydrogen present on the earth and this would cause the liberation of between 1.8 and 2.4×10^{26} calories.

In the second case, heat would be absorbed since the reaction is accompanied by a gain in mass. Here the quantity of heat absorbed would be of the order of 10^{26} cal.

Beside this amount of heat the heat liberated by the formation of molecular hydrogen and water (approximately 10^{30} calories) and the amount of heat required for geological processes (also about 10^{30} calories) is negligible.

¹ Proc. Roy. Soc., 115, 487-515 (1927).

² Nature, 108, 584.

The amount of helium required for the formation of the elements of higher atomic weight than that of nickel is about 4.8×10^{26} grams and since the formation of one gram of helium from radium causes the emission of $226/4 \times 3.7 \times 10^9$ cal., it may be assumed that the formation of these more complex elements would absorb $226/4 \times 3.7 \times 10^9 \times 4.8 \times 10^{26}$ cal. or 1×10^{37} calories.

The formation of 4.8×10^{26} grams of helium from hydrogen would evolve $4.8 \times 10^{26} \times 1.6 \times 10^{11}$ cal. or about 7.7×10^{36} cal.

Summing up we have the following possibilities

| | Case I | Case II |
|----------------------------------------------------------------|------------------------|--------------------|
| Disintegration of even-numbered elements | 2×10^{36} cal | $- 10^{36}$ cal |
| Formation of elements of high atomic weight | $- 10^{37}$ | $- 10^{37}$ |
| Formation of helium required for these elements from hydrogen | 8×10^{36} | 8×10^{36} |
| Formation of molecular hydrogen and water | 10^{30} | 10^{30} |
| Energy absorbed by geologic processes and radiated into space. | $- 10^{30}$ | $- 10^{30}$ |

Obviously there is no way of making these quantities of heat balance at present.

The Formation of Magmas

Although this hypothesis is not, in its present state, ready for application to geological theory, there is no doubt but that it could easily be applied. One of the geologic processes for which no good explanation has been advanced is the formation of magmas which contain juvenile water. According to the hypothesis of radioactive disintegration within the crust, it is possible to explain the formation of a magma by the heat of disintegration only if we assume an increase in radioactive material at depth. This, as has already been pointed out, seems to be an assumption without much foundation and does not explain satisfactorily the presence of water in the magma. According to the present hypothesis, there is no scarcity of material undergoing disintegration since it includes the even-numbered elements of low atomic weight which make up over 85% of the earth's crust and increase towards the central core of which they make up approximately 99½%. Owing to the fact that the material undergoing disintegration occurs in the form of oxides, since very few intrusions contain native metals, and since the odd-numbered elements formed have a lower valence than do the even-numbered elements from which they are derived, oxygen is made available as what might be called a by-product of the disintegration and this oxygen can combine with the hydrogen liberated to form water. The presence of the water reduces the melting point of the rocks with which it is associated and there is a great excess of heat in the neighborhood of the disintegrating elements in any case, so fusion is easily explained.

The writer does not believe, however, that the batholiths and other results of the formation and rise of molten rocks come directly from the area

in which the disintegration takes place without being greatly modified by other processes. It is conceivable that masses of almost continental size form the parent magma and that differentiation through gravitative adjustment results in the drawing off of the lighter constituents of this magma and their concentration in smaller reservoirs from which they begin to move towards the surface. Meanwhile, the larger mass beneath solidifies and disintegration begins afresh to result in the formation of another magma at a later time from which the differentiates may again move upwards following either the path of the earlier intrusions or another path.

Naturally the rising magma may be greatly modified by assimilation and there will certainly be further differentiation with the splitting off of subsidiary masses.

Owing to the fact that nothing can be stated regarding the rate of disintegration, and nothing is known as to the amount of heat evolved, the size of the original masses of magma, or their depth, or the rate of flow of material towards the surface it is useless to speculate regarding the length of time that elapses between the formation of magmas in any one area. It is evident, however, that there will be a certain periodicity to the process and also that the interval between the periods of activity will be extremely long. Whether or not this interval is the interval between revolutions on the earth's crust cannot be stated definitely, but it seems reasonable to believe that this is the case.

The hypothesis, therefore, falls into the same category as a number of hypotheses at present employed in geological theory. Like the others, it would explain a great deal if we had sufficient data. Before going farther and developing an imposing structure on such a foundation, the writer presents the foundation alone in the hope that it will be considered from a physical and chemical standpoint in order to find out whether or not it will stand.

Acknowledgments

This paper was examined in manuscript by Dr. A. L. Day and Dr. H. S. Washington of the Geophysical Laboratory, and Professors W. A. Noyes and Jakob Kunz of the University of Illinois in order that any major errors might be detected. The writer wishes to acknowledge with deep gratitude the assistance afforded by these gentlemen without in any way implying that they consider the hypothesis more than an interesting speculation.

BEHAVIOR OF ZINC OXIDE AND ZINC OXIDE-CHROMIUM OXIDE CATALYSTS IN THE DECOMPOSITION AND SYNTHESIS OF METHANOL*

BY H. H. STORCH

Introduction

The search for a catalyst which will accelerate a given reaction is frequently conducted by studying the action of the prospective catalyst on the desired product. This procedure, while thermodynamically sound, does not always give conclusive results. This is especially true when mixed catalysts are being tested in the decomposition of a single substance which it is desired to synthesize from two reactants. Comparatively little work has been done on the action of mixed or promoted catalysts on the decomposition or transformation of a single substance. Unless the adsorption at the interfaces of mixed or promoted catalysts is different (quantitatively, at least) from the adsorption of simple catalysts, it is difficult to account for promoter action in the decomposition of a single substance.

Palmer¹ found that magnesium oxide and manganous oxide promote copper as a catalyst for the dehydrogenation of ethanol, provided that these promoters are present in amounts greater than 2.5 and 0.4 atomic percent, respectively. Smith and Hawk² found that zinc oxide, (prepared by precipitation with sodium carbonate from zinc nitrate solution, followed by drying and heating to form the oxide), was of the same activity in the decomposition of methanol as their most active ZnO-Cr₂O₃ preparation. Indeed, these authors found that the addition of chromium oxide in any proportion other than 8 ZnO-1 Cr₂O₃ resulted in a catalyst markedly less active than the most active zinc oxide catalyst.

During the course of a research not primarily concerned with the purposes of this paper, some data on the behavior of zinc oxide and zinc oxide-chromium oxide catalysts in the decomposition of methanol were obtained in this laboratory by A. W. Gauger, and in the synthesis by the writer.

Methanol Decomposition

Methanol was heated in a copper container immersed in a water-bath. The flow of vapor from this container was controlled by means of a brass valve, from which the methanol passed through a flowmeter kept in an oven at 100°C, and thence into the catalyst chamber. The latter consisted of a Pyrex U-tube heated by means of an electrical resistance furnace.

The gases and vapors from the catalyst passed through a condenser immersed in a methanol-solid CO₂ bath, thence through two water scrubbers,

* Contribution from the Research Laboratory of the Roessler and Haslach Chemical Co., Perth Amboy, N. J.

¹ Proc. Roy. Soc., 101A, 175 (1922).

² J. Phys. Chem., 32, 420 (1928).

and finally through a flow-meter. The off-gases were, unfortunately, not analyzed. The percent decomposition was calculated from the amount of methanol recovered.

The catalysts were prepared as follows:—

(1) 200 grams of zinc oxide¹ were mixed with 22 grams of chromic acid, and enough water added to form a thick paste. 100 grams of 4-8 mesh pumice were mixed with the paste, and the mixture dried at 150°C.

(2) 242 grams of zinc carbonate were dissolved in formic acid, and the solution mixed with 50 grams of asbestos. The mixture was evaporated to dryness, and dried at 150°C.

Both catalysts were treated at 200°C with hydrogen saturated with methanol at room temperature, for several hours before use.

TABLE I
Methanol Decomposition

| Catalyst No. | Wt. grams | Apparent Volume cc. | Temp. °C. | Space Velocity per hour | % Decomposition |
|--------------|-----------|---------------------|-----------|-------------------------|-----------------|
| 1 | 185 | 543 | 300 | 110 | 3 |
| 1 | 185 | 543 | 365 | 110 | 80 |
| 2 | 193 | 400 | 300 | 111 | 4 |
| 2 | 193 | 400 | 342 | 108 | 78 |

It will be observed from Table I, that these catalysts were of approximately equal activity. Catalyst No. 2 was of greater apparent density than No. 1, and because of this and the difference in the character of the supports used, a rigorous comparison of the data is not permissible. However, if the large increase in activity usually associated with promotion existed, a much greater variation in the percent decomposition would have been observed.

Synthesis of Methanol

The earliest published work on the use of zinc oxide (per se) as a catalyst for methanol synthesis was that of Patart.² Using "pure" zinc oxide as a catalyst at 400-420°C, and 150-200 atmospheres pressure of 2H₂ + 1 CO, the liquid condensate was of 0.896 specific gravity at 19°C, and contained about 80% methanol, the bulk of the remaining 20% being water. The data given are insufficient to calculate space velocity or space-time-yield. The method of preparation of the catalyst is not described. An equally laconic reference to the use of zinc oxide was published in a description of experiments at the Badische Anilin und Soda Fabrik.³ Dreyfus⁴ also mentions the use of zinc oxide. Woodruff and Bloomfield⁵ state: "Zinc oxide—per se—has no catalytic effect on the methanol reaction."

¹ Baker's C. P. chemicals were used without further purification.

² *Chimie et Industrie*, 13, No. 2, 182 (1925).

³ *Die Metallbörse*, 48, 1317 (1925).

⁴ Eng. Pat. 262, 494 (1926).

⁵ U. S. Pat. 1,608,643 (1926).

Zinc and chromium oxides are separately listed by Mittasch and Schneider¹, and the mixed catalyst specifically claimed for methanol synthesis by Mittasch and Pier.²

The data given below on the synthesis of methanol were obtained by using $4\text{H}_2 + 1\text{CO}$ gas at 3000 lbs. pressure. The reactants were prepared passing "blue water-gas" (obtained from an ordinary water-gas generator) mixed with steam over a water-gas shift catalyst so that the H_2/CO ratio was changed from about 1.1 to 1.9. After scrubbing with caustic soda solution, the gas was diluted with electrolytic hydrogen until a ratio of $4\text{H}_2/1\text{CO}$ was obtained.

The reaction vessel was made of chrome-vanadium steel, and was lined with copper, heating being accomplished by an electric furnace surrounding the converter. The volume of the catalyst space was 42 cc. The catalyst temperature was measured by means of a concentric thermocouple³ imbedded in the catalyst. The temperature of the furnace was controlled by a Walton Torrey thermoregulator.

The converter off-gases were led into a pressure condenser, and thence at atmospheric pressure to a gas meter.

Table II gives the results obtained using zinc oxide catalysts and catalyst No. 1 ($\text{ZnO-Cr}_2\text{O}_3$). The latter was prepared as described above, except that the pumice was omitted, and the catalyst used in the form of a fine granular powder. The preparation of the various forms of zinc oxide is described below. All of these were used as granular powders of approximately the same screen analysis as Catalyst No. 1. All tests were made after the catalyst had been treated with $9\text{H}_2 + 1\text{CH}_3\text{OH}$ at 300°C for 12 hours.

TABLE II
Methanol Synthesis
Space Velocity per hour = 4000 in all cases

| Catalyst No. | Temp °C. | Space Time Yield ⁴ |
|--------------|----------|-------------------------------|
| 1 | 33° | 660 |
| 3 | 33° | 360 |
| 3A | 33° | Inactive |
| | 35° | " |
| 3B | 33° | 290 |
| 3C | 33° | Slightly Active |
| | 35° | 88 |
| 3D | 33° | 360 |

The product obtained was in all cases better than 95% methanol by volume. Each of the space-time-yield figures represents an average value taken for determinations made about once per hour for at least three hours

¹U. S. Pat. 1,201,850 (1916).

²U. S. Pat. 1,558,559 (1925).

³This was a copper-constantan couple made by passing an electrically insulated constantan wire thru a piece of copper tubing and welding at one end. The other end was silver soldered into a threaded brass spindle. The latter was screwed into a T attached to the stem of the converter, the reactants being admitted thru the other end of the T.

⁴S. T. Y. = lbs. of CH_3OH per cubic foot of catalyst per 24 hours.

and in some cases (Catalyst No. 1, and No. 3) the tests were prolonged to 200-300 hours. The average deviation from the mean S.T.Y. varied for the different catalysts from 5% to 10%.

Preparation of Zinc Oxide Catalysts

(No. 3) 200 grams of zinc oxide were mixed with one liter of water, and sufficient concentrated nitric acid added to dissolve the oxide. An excess of ammonia was added to form $\text{Zn}(\text{NH}_3)^{++}$. 200 grams of NaOH dissolved in 500 cc. of water were added, and the mixture boiled until no odor of ammonia could be detected. After filtration and washing (until no test for nitrates was obtained in the wash waters), the filter cake was dried at 200°C.

(No. 3A) 200 grams of zinc oxide were mixed with one liter of water, and an equivalent quantity of concentrated nitric acid added. 600 grams of 28% ammonia were added, and the resulting mixture filtered. The filter cake was washed and dried as in No. 3.

(No. 3B) Identical with preparation of No. 3, except that the addition of ammonia was omitted.

(No. 3C) Zinc formate was prepared in the form of a fine crystal powder.

(No. 3D) 81 grams of zinc oxide were dissolved in one liter of a dilute acetic acid solution containing 120 grams of acetic acid. A solution of 171 grams of $\text{Ba}(\text{OH})_2$ in two liters of water was mixed with the zinc acetate solution and the mixture filtered. The filter cake was washed until no test for acetates was obtained in the wash waters, and subsequently dried at 200°C.

Of two preparations of chromium oxide catalysts, one made by soaking pumice in molten CrO_3 , and the other by precipitation of $\text{Cr}(\text{OH})_3$, the latter was found to be only slightly active (about 20 S.T.Y. at 330°C), and the former inactive.

The slight activity of chromium oxide, combined with the fact that the most active zinc oxide catalysts gave only about 50% of the yield obtained from the $\text{ZnO-Cr}_2\text{O}_3$ catalyst, indicates that the $\text{ZnO-Cr}_2\text{O}_3$ interfaces enhance the activity of zinc oxide in methanol synthesis. The fact that no such increase in activity is observed in the decomposition of methanol may be due to the fact that the experiments on the decomposition were made at atmospheric pressure instead of at the partial pressure corresponding to the conditions in the synthesis. However, it seems improbable that twenty atmospheres pressure of CH_3OH would change the primary adsorption characteristics of either ZnO or $\text{ZnO-Cr}_2\text{O}_3$ catalysts.¹

Regarding the mechanism of the synthetic reaction very little can be stated, because of insufficient data. The variation of the space-time-yield with space velocity (see Table III) is characteristic of any contact reaction

¹ This statement is based upon the work of Palmer and Constable (Proc. Roy. Soc. 98A, 13, (1920); 99A, 412 (1921); 101A, 178 (1922); 106A, 250 (1924); 107A, 255, 270 (1925); 108A, 355 (1925)) who showed that the rate of dehydrogenation of ethanol is independent of the pressure. This is due to the fact that the reaction proceeds in a unimolecular layer on the catalyst surface. It is probable that catalysts for the decomposition of methanol would be similarly unaffected by an increased pressure of CH_3OH .

in which the conversion is relatively high, and hence the data are insufficient to indicate whether the adsorption of the methanol formed retards the synthesis.

TABLE III
Space-Velocity:
Space-time-yield Relationship

| Space velocity per hour | Space time yield | % Conversion of CO to CH ₃ OH |
|----------------------------|---------------------|---------------------------------------------|
| 2180 | 476 | 52 |
| 2430 | 500 | 50.5 |
| 2860 | 566 | 46 |
| 4080 | 663 | 40 |
| 4550 | 790 | 41 |
| 5480 | 900 | 38 |
| 5520 | 874 | 39 |
| 7850 | 1110 | 33 |
| 7900 | 1120 | 33 |
| 8260 | 1230 | 30 |
| 11600 | 1450 | 30 |
| 13500 | 1530 | 27 |
| 14900 | 1535 | 24.5 |
| 17000 | 1660 | 23 |
| 19200 | 1910 | 23.5 |
| 25300 | 2260 | 21 |

No data on the change of S.T.Y. with pressure are available for this catalyst. The change of S.T.Y. with temperature is complicated by the extraordinarily narrow range of temperature in which Catalyst No. 1 may be used without deterioration due to sintering. Thus this catalyst is practically inactive at temperatures appreciably below 300°C, and at 350°C the S.T.Y. is lower than that obtained at 330°C. Rapid measurements at 350°C indicate a somewhat larger yield than at 330°C.

The author wishes to express his appreciation of helpful criticisms made by Dr. B. S. Lacy who directed the research in the course of which the above data were obtained.

Summary

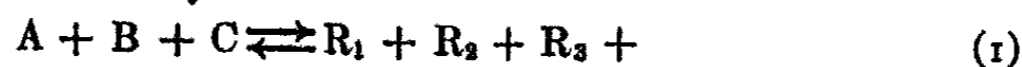
The addition of chromium oxide to a zinc oxide catalyst in certain proportions increases the activity of the catalyst for methanol synthesis, but does not affect its activity for methanol decomposition (at atmospheric pressure).

Some data describing the characteristics of a ZnO-Cr₂O₃ catalyst in the synthesis of methanol are given.

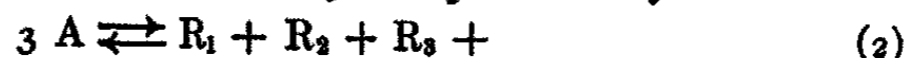
CHEMICAL REACTIONS OF THE THIRD ORDER*

BY FRANK E. E. GERMANN

The general form of stoichiometric equations for reactions of the third order may be represented by



A special case of a third order reaction may be represented by



which states that three molecules of A react in such a way as to give the products on the right side of the equilibrium equation.

According to the principle of the mass action law, we may write in the first case

$$-\frac{d(a-x)}{dt} = -\frac{d(b-x)}{dt} = -\frac{d(c-x)}{dt} = k(a-x)(b-x)(c-x) \quad (3)$$

or
$$dx/dt = k(a-x)(b-x)(c-x) \quad (4)$$

in which a , b and c represent the initial concentration in mols per liter of A, B and C respectively present in the solution at zero time. x therefore represents the mols per liter of each compound, A, B and C, which have disappeared at time t .

In the same way, we may write for the second case

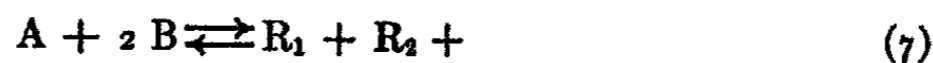
$$-\frac{d(a-x)}{dt} = \frac{dx}{dt} = (ka-x)^3 \quad (5)$$

This is also the form assumed in the first case, if the initial concentrations of A, B and C are equal. If, however, $a \neq b = c$, that is, if the initial concentrations of B and C are identical, but different from A, we have

$$dx/dt = k(a-x)(b-x)^2 \quad (6)$$

Up to this point the discussion is equally valid whether we speak in terms of mols or equivalents per liter.

Suppose now we have a third order reaction of the form



If we are using equivalents per liter as the measure of concentrations, then we have

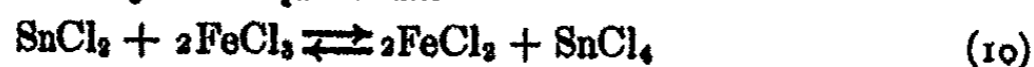
$$dx/dt = k(a-x)(b-x)^2 \quad (8)$$

which is identical to (6). If, however, we are expressing our concentration in terms of mols per liter, it is obvious from the equation that two mols of B disappear for every mol of A that disappears. We must, therefore, now write

$$dx/dt = k(a-x/2)(b-x)^2 \quad (9)$$

* Contribution from the Department of Chemistry of the University of Colorado by Frank E. E. Germann.

A particular case of an actual reaction which was first carefully studied by Noyes¹ is represented by the equilibrium



Since Noyes expressed concentrations in terms of equivalents, he made use of equation (8), which on integration yielded

$$k = \frac{1}{t} \cdot \frac{1}{(a-b)^2} \left\{ \frac{(a-b)x}{b(b-x)} + \ln \frac{a(b-x)}{b(a-x)} \right\} \quad (11)$$

The tendency at the present time is to make use of mols per liter in expressing all concentrations, since there is less danger of confusion. As a result, many errors have crept into treatises on chemistry, and as a necessary consequence, into the research work of the unsuspecting. Thus we find² in Getman's "Outlines of Theoretical Chemistry" the statement, "The following table gives the results obtained with 0.025 molar solutions of ferric chloride and stannous chloride." As a matter of fact the table is a copy of Table 6 of Noyes taken from page 551 of the article referred to above, except for the fact that Noyes expressly labels his concentrations as "0.025 normal" in place of "0.025 molar" as given.

In connection with the same reaction,³ Taylor⁴ states specifically that concentrations are expressed in mols per liter and goes on to state (referring to the equation of the form of equation (1)) "If the initial concentrations of A and B are equal, or if the stoichiometric equation has the form $2A + C =$ one or more resultants, we have

$$dx/dt = k(a-x)^2(c-x) \quad (12)$$

whence

$$k = \frac{1}{t} \cdot \frac{1}{(c-a)^2} \left\{ \frac{(c-a)x}{a(a-x)} + \ln \frac{c(a-x)}{a(c-x)} \right\} \quad (13)$$

This is correct for the case of $a = b$, but not for the case of $2A + C = R_1 + \dots$ Obviously equation (12) in the case of concentrations expressed in mols per liter, should be replaced by

$$dx/dt = k(a-x)^2(c-x/2) \quad (14)$$

which is of the form of equation (9), and (13) should be replaced by the integrated form of equation (14).

Although equations of the forms of (9) and (14) may have been used and integrated in the past, they have successfully escaped the attention of the writer. It may, therefore, be of interest to develop this point more fully. For integration, equation (8) may be written

$$k \int dt = \int \frac{dx}{(a-x)(b-x)^2} \quad (15)$$

Similarly, equation (9) may be written

¹ Noyes: *Z. physik. Chem.*, 16, 546 (1895).

² Getman: 4th Edition, p. 433 (1927).

³ Taylor: "A Treatise on Physical Chemistry," 2, 872.

⁴ Chapter written by Francis Owen Rice.

$$k \int dt = \int \frac{dx}{(a - x/2)(b - x)^2} = 2 \int \frac{dx}{(2a - x)(b - x)^2} \quad (16)$$

It is, therefore, obvious that if equation (11) gives the value of k as derived from equation (8), we have only to transform (11) by introducing the factor 2 in the numerator and replace a by $2a$ to obtain a value of k from equation (9). Thus we have

$$k = \frac{2}{t} \cdot \frac{1}{(2a - b)^2} \left\{ \frac{(2a - b)x}{b(b - x)} + \ln \frac{2a(b - x)}{b(2a - x)} \right\} \quad (17)$$

Similarly the equation at the bottom of page 872 in Taylor should read

$$k = \frac{2}{t} \cdot \frac{1}{(2c - a)^2} \left\{ \frac{(2c - a)x}{a(a - x)} + \ln \frac{2c(a - x)}{a(2c - x)} \right\} \quad (18)$$

In all other cases of 1st, 2nd and 3rd order reactions, the equations developed for k are equally valid whether mols or equivalents are used. The numerical value of k will naturally depend on the units chosen. When working with orders higher than the third, the equations will, in general, be different for concentrations expressed in equivalents or in mols. No attempt has been made in the above to distinguish between different values of k by means of different symbols.

Under the date of February 14, 1928, Dr. F. O. Rice called the attention of the author to an error of the above type in Bodenstein's article, (*Z. physik. Chem.*, 29, 677 (1899)) in which the reaction



was under consideration.

This error was pointed out and critically examined by Wegscheider: *Z. physik. Chem.*, 35, 580 (1900); but no formula for k was given which can be readily compared with equations (17) or (18).

NEW BOOKS

A Comprehensive Survey of Starch Chemistry. By R. P. Walton, Editor. Vol. I. 26 × 18 cm; pp. 360. New York: Chemical Catalog Company, 1928. Price: \$10.00. "This symposium is intended to be a presentation of the various phases of starch chemistry and technology. . . . The mechanism of starch transformation is of primary interest in such universal processes as the baking, brewing, and fermentation industries. The conversion of starch to glucose by acid hydrolysis represents an industry which is a significant factor in the world's food economy. The material, starch itself, is of considerable industrial importance; as one of the most abundant of naturally occurring organic substances, starch constitutes an inexpensive raw material whose versatility of characteristics permits its extensive application in many manufacturing processes," p. 5.

The volume is divided into two parts, the first being the symposium mentioned in the preceding paragraph. There are nineteen articles: Thermal Depolymerization of Starch in Relation to Molecular Constitution by Amé Pictet; Methylation of Starch in Relation to Molecular Constitution by Sir James Irvine; Enzymic Hydrolysis of Starches in Relation to Molecular Constitution by A. R. Ling; Bacterial Degradation and Constitution of Starch by Hans Pringsheim; The Colloid-Chemical Properties of Starch by Max Samec; Non-Carbohydrate Constituents as a Factor in the Characterization of Starch Components; The X-ray Spectrography of Starch by J. R. Katz; Chemical Nature of Certain Amylases by H. C. Sherman; The Role of Starch in Bread-making by C. L. Alsberg; Gelatinization and Retrogradation of Starch in the Bread Staling Process by J. R. Katz; Conversion of Starch in the Fermentation Industries by Auguste Fernbach; Manufacture of Corn Starch by G. M. Moffett; Manufacture of Potato Starch by Eugen Preuss; Manufacture of Dextrin, Envelope Gums, British Gum, and Modified Starches by V. G. Bloede; Starch and Flour Adhesives by Jerome Alexander; Significance of Starch Viscosity in the Manufacture of Paper and Textiles by W. A. Nivling; The Use of Starch in the Textile Industry, particularly for the Sizing of Cotton Warps by F. D. Farrow; Starch-converting Enzymes used in the Textile Industry by H. C. Gore, H. G. Tarley, Leo Wallerstein and Jokichi Takamine, Jr.; Early Development of Starch Chemistry by R. P. Walton.

When heated in glycerol the following changes occur: starch → soluble starch → hexahexosan → trihexosan → α-glucosan, p. 11. Glucosan is converted into glucose by boiling with water. Irvine considers that "there is no essential difference between the constants of a 'pure' maize-starch and a 'pure' glycogen; the same resemblance extends to the acetates and methylates of these polysaccharides and, as already stated, the methylates give the same hydrolytic products. There can be no reasonable doubt that starch and glycogen, when freed from extraneous constituents, are chemically identical," p. 23. Starch and glycogen vary, however, "in their capacity to combine with nitrogen, phosphorus, and metallic radicles. In particular, the tenacity which glycogen retains combined iron seems to differentiate the compound from starch."

Pringsheim says, p. 36, that diamylose and triamylose form true solutions in cold water but undergo transition to the colloidal state in boiling water. On p. 40 he writes that "animal starch or glycogen is apparently the only other substance besides starch, which is fermentable by *Bacillus macerans*. We have found this carbohydrate to be identical with amylopectin, and, like it, to form a relatively large proportion of β-hexaamylose."

"The relations between glycogen and lactic acid are known to be of great importance to the energy of muscles. Except glycogen only starch, which as we have seen has the same carbohydrates in its hull substance as glycogen, can be glycolyzed; with amylose the reaction is somewhat retarded. The condition for the possible transformation of a polysaccharide into lactic acid is obviously that its molecule is changeable exclusively into the characteristic γ-glucose residues as formulated by us. This, as Meyerhof has shown, with starch derivatives which we supplied, both hexosans are glycolyzed, but this is not the case with amylobiose and amylotriose although the suitability of the latter for amyolysis has not

been destroyed. Hence we consider that the sugar phosphoric esters likewise exhibit the γ -glucose structure of our radical for they alone, besides the starch components and hexosans, are converted into alcoholic yeast fermentation and are formed by the muscle enzyme in glycolysis," p. 45.

Samec stresses the importance of phosphoric acid in starch, p. 52. "In contrast to starch solutions, the intact starch granules do not give off any appreciable quantities of electrolytes. By treatment with dilute HCl, followed by a thorough washing with water, the cations can be removed with relative ease. Phosphoric acid, however, is retained in the starch granule, so that after a drastic washing process the starch ash consists almost entirely of phosphoric acid. In order to remove this also, the starch granule must be dissolved, the dissolved substance separated in some manner from the solution, the coagulum again dissolved and so on; there finally results an almost completely electrolyte-free starch, whose principal organic characteristics correspond to those of the native starch, although it is no longer capable of gelatinization.

"The three processes: aging, heating under pressure, and demineralization, produce one effect in common, that is, the transition of a gelatinizing starch form into one incapable of gelatinization, with the concomitant cleavage of phosphoric acid.

"On the one hand, this acid appears to be firmly combined with the starch, although it still acts as a dibasic acid (for example, against phenolphthalein and methyl orange). But on the other hand, it can be hydrolyzed by hot water, so that it appears in all probability that the starch and phosphoric acid are combined in an ester linkage. According to this hypothesis, amylopectin is a starch-phosphoric acid ester.

"To support this theory it was necessary, above all, to show that there was an unequal distribution of phosphorus in the starch components, termed by L. Maquenne, amylose, and amylopectin. According to the procedure of Z. Gatin-Gruzewska, I prepared a portion of amylose and of amylopectin from potato starch and purified both of these by repeated dialysis against distilled water. The results actually obtained showed 0.185% P_2O_5 in the amylopectin portion and 0.007% P_2O_5 in the amylose portion.

"The separation of amylopectins from amyloses is much more easily and thoroughly accomplished by a suitable process of electro dialysis. By this method, the amylopectin separates as a colloidal electrolyte in the form of a slime layer, the amyloses remain in solution, can be pipetted off and the amylopectin can be washed by decantation with water. Since there is also a migration of all the associated electrolyte which is not combined, a material is obtained with relative rapidity and ease which is suitable for the determination of inorganic associated substances.

"The amylopectin fractions of different starch varieties were separated. It was noted that these differed not only in the relative percentages present in the starch, but also in appearance, in the manner in which they responded to electro dialysis, in their conductivities and in their phosphorus content. In spite of all these differences, however, one absolute relation could be observed; the viscosity of a starch solution always depends on the relative quantity of amylopectin present in the starch.

"As physico-chemical methods have already indicated, the phosphoric acid ester of starch is hydrolyzed when heated with water under pressure. If starch suspensions are heated under pressure for various periods of time and then entirely freed from uncombined electrolytes by dialysis and electro dialysis, it is demonstrated that the longer the duration of the heating the lower becomes the phosphorus content of the starch material. In order to establish conclusively the ester nature of amylopectin it was necessary that, by synthesis, I should again obtain a gelatinizing product upon esterification of the phosphorus-free starch substance with phosphoric acid. The first step in this procedure, naturally, was to obtain that portion of the carbohydrate which was combined with phosphoric acid in the native starch. To this end, I first removed the amylose fraction by electro dialysis, washed out the amylopectin very thoroughly with water and then, by heating with water, decomposed it into phosphoric acid and the organic component. After removal of the free phosphoric acid, the substance was phosphorylated with phosphorus oxychloride according to the method of C. Neuberg. All operations were conducted so as to prevent any peptization

or hydrolytic degradation of the starch substance. After suitable purification, I obtained a perfectly clear, highly viscous product, which, in general, resembled the natural amylopectin, exhibiting, however, a considerably higher viscosity and P_2O_5 content. All typical properties which the starch solution had lost by heating with water had been restored. The highly viscous solution conducts the electric current very well, migrates rapidly and integrally to the negative pole in an electrical field, separates on electro dialysis as a gelatinous layer and is very easily precipitated by alcohol in the form of a gummy mass.

"The successful synthesis of amylopectin in potato starch was also repeated with other starch varieties. The result was the same; in all cases I succeeded in obtaining analogous products which formed stiff pastes. In one respect this helped to solve the problem of differentiating starches according to their technical value.

"The assertion that starch, which had been regarded as a pure carbohydrate, exhibits many of its typical properties only when esterified with phosphoric acid, was at first received with some skepticism. The experiments which I had carried out, however, in the course of years were verified by a number of independent methods and all the essential points definitely established."

"The view that the gelatinizing ability of a polysaccharide is dependent upon or at least considerably increased by coupling with a polybasic acid, has later been established with other plant materials. C. Neuberg, using analytical methods, and M. Samec, using colloid chemical methods, both found that the jelly-forming component of Agar was composed of an Agar-sulphuric acid combination," p. 54.

"Certain products of wheat starch, peptized by means of ultraviolet light, migrate to the cathode, although they do not contain any metallic ions. Also the amyloses which are free from electrolyte, and especially the amylopectin, have a pronounced negative charge. This electrical charge could only be explained on the assumption that starch was combined with a protein-like substance and the importance of nitrogen in starch was thereby explained," p. 57.

"The color given with iodine is dependent neither on the mean molecular weight, on the state of hydration, on the combination with phosphoric acid, nor on the presence of reducing groups in the molecule. The cause for the difference in iodine color is much more likely to lie in the organic constitution or at least in the structural combination of the molecular aggregates of the carbohydrate. . . . The idea that this was due to a difference in constitution received support on the one hand through the work of H. Pringsheim, and on the other hand through the results of A. R. Ling and D. R. Nanji. The former was able to break down the organic components of amylopectin to a trisaccharide, where, with the amyloses (which give a clear blue coloration with iodine), only disaccharides could be obtained by the same method. A. R. Ling and D. R. Nanji sought the cause for the difference in the starch components in the different distributions of α - and β -linkages in a hexasaccharide, which they considered to be the basic constituent of starch. W. von Keufman also considered the structure of the carbohydrate to be influential in determining its color with iodine. According to him, the presence of oxygen rings necessitated a blue coloration, whereas the correspondingly greater hydroxylated compound should give a red color," p. 58.

Samec suggests calling the substances which give a blue color with iodine amyloamyloses, amyloextrin, and amyloextrinic acid, depending on whether they are reducing, non-reducing, or acidic. The corresponding substances which give a red color with iodine he calls erythroamyloses, erythroextrin, and erythroextrinic acid. Those which give no color with iodine should be known as achroamyloses, achroextrin, and achroextrinic acid, p. 59.

"The existence of such substances as we now call enzymes first became known through the observation that barley malt had the property of hydrolyzing starch. Since this must have been due to something previously unknown but contained in the malt, a concentration was later sought by fractionating the malt in different ways, testing the fractions, rejecting those which did not show the peculiar property, and fractionating still further those in which it appeared. The principle is well illustrated in the now classical investigations which led to the isolation of radium," p. 78.

"In strong and in weak flours the starch is distributed differently. Anyone who has taken the trouble to examine both kinds under the microscope, knows that, while the starch granules are similar except in size, they bear different relations to the gluten. In a hard-wheat flour the gluten is present in relatively large masses in which the greater part of the starch is imbedded. The number of starch granules that are to be seen lying free is relatively small. In soft-wheat flour the gluten masses are smaller and carry imbedded in them correspondingly less starch. A relatively large proportion of the granules lies free. Hence in a strong flour the water must diffuse through a layer of gluten before it can reach the majority of the starch grains, while in a weak flour it can reach most of them directly. It is therefore quite possible that in dough made from strong flour by the ordinary process of kneading the starch granules never become fully saturated with water or else become so only gradually as fermentation progresses, whereas in weak-flour doughs the starch grains become fully saturated almost immediately. Possibly one of the effects of the high-speed mixer is to hasten saturation of the starch granules and thus to contribute to the better absorption effected by these machines. It is obvious then that the quantity of starch in a flour and perhaps its freedom probably play a rôle in determining absorption, even though a minor one as compared with the gluten," p. 90.

"I have been able to discover, further, that bread staling is the result of a change which is caused by cooling of the bread and which does not take place if the cooling is prevented. This process proceeds at a considerably slower rate than the cooling itself, and indeed, if bread is kept at a temperature of 60°C or over and if loss of moisture and condensation of water are prevented, the bread, theoretically, can be kept fresh for indefinitely prolonged periods; bacterial conversions, however, must be excluded by the addition of a disinfectant. It has been an empirical fact known to bakers for a long time that bread crumb can be refreshed by heating the bread, and that this process may be repeated several times until the bread has lost too much moisture. Boussingault confirmed the correctness of this old, practical experience by a number of tests. He found that the process of refreshing bread could be repeated any number of times, say seven times, if the bread crumb is kept in a glass cylinder closed by a properly-fitting stopper so that all losses of water are prevented. My experiments have demonstrated that changes are precluded almost entirely if the crumb is not allowed to cool. Hence, a physico-chemical equilibrium must exist between fresh and stale bread; the two forms exhibit the same behavior as allotropic states of the same substance. The question here is whether we are dealing with a homogeneous or a heterogeneous equilibrium. In the former case, there should not be a sharp change but rather a gradual transition between the temperatures at which bread stays fresh and those at which it becomes stale. In the second case, there should be a precise temperature value where the change occurs. Above this temperature the fresh form of the bread would be the state of equilibrium, while below this temperature the stale state would be that of equilibrium. On making a test in this connection it was ascertained that a gradual change or transition took place. For these experiments, relatively large pieces of bread crumb were kept in a thermostat at different temperatures for 24 or 48 hours under conditions which strictly prevented all losses of moisture and condensation of water. The degree of staling was then determined by means of three methods. . . .

"By all of these three methods it was concordantly shown that, at 60°C and over, bread retains its freshness entirely, that at about 40°C it becomes approximately half stale, that at 30°C it is still more so, and that at 17° and 0°C it becomes totally stale. The degree of staling of a piece of bread crumb kept for 24 or 48 hours may be represented graphically by a continuous curve as a function of the temperature. There is no sharp break or transition point and, apparently, a homogeneous state of equilibrium prevails. This finding is confirmed by the fact that, upon microscopic examination, nothing indicative of the formation of a precipitate in or between the starch granules can be observed. If a heterogeneous state of equilibrium prevailed the occurrence of such a precipitate would be expected," p. 101.

"When the humidity is 85 percent or more the crust rapidly loses its crispness. Maintained in an atmosphere of greater dryness, the crust, to be sure, remains crisp, but the layer

of crumb directly underneath the crust is caused to dry out. Hence, a current of air must be used whose humidity is so regulated that neither the one nor the other defect or condition arises. This air current will then carry off regularly all such water as may diffuse from the crumb into the crust. Now, it was found as a matter of fact, that there is a significant interval between these two difficulties and that the interval ranges between 65 and 75 per cent atmospheric humidity. The rate of air flow must be commensurate. By this unique method, bread baked at night could be kept fresh so that it could be sold the next morning as fresh bread without complaints from the public.

"An Amsterdam baker in 1915 offered to have tests made in his shops, that is, at a time when night work in bakeries had not yet been prohibited. He baked his bread in the course of the evening, and after it had been fairly cooled, he then placed it in a large cabinet constructed along the above lines and in which a current of air was maintained all night by means of an exhauster. The humidity of the air current was maintained at the above-mentioned figure by contact with a solution of calcium chloride, the original concentration of the latter being restored every day to its original value.

"The fundamental principle of the whole method and the main condition upon which its success depends is that bread, cabinet and air should be at the same temperature. This point must be satisfied with sufficient exactness if the method is to be successful, otherwise water will be conveyed from points of higher temperature to those of lower temperature. Whenever difficulties were encountered in practical working, these were nearly always due to a failure to strictly observe the above condition.

"It was found that the baker above referred to was enabled to sell bread, kept fresh in this manner, to the public in the early morning hours without complaints having been made on the public's part. These experiments were made with strict compliance to the Dutch industrial inspection laws.

"Practical introduction in Holland, unfortunately, was frustrated by the law prohibiting night work by bakers, the law becoming effective shortly after this time. The power of laborers' unions had grown to such a point that this law could be passed in spite of its injury to the public at large. No fresh bread can be sold at all before 10 A. M. and in view of this situation, the above working method offers no inducements to bakeries.

"However, it is very desirable that tests should be made in other countries in order to determine whether the various methods of preserving bread in fresh condition could be utilized with advantage from economical or social standpoints. Since bread is a product varying widely in different countries, as pointed out above, and since the demands of the public are different, it will be necessary to make experiments in each country before it is possible to draw an absolutely definite conclusion for that country," p. 116.

"It has been known for a long time from practical experience that persons with delicate digestive organs can digest stale bread much more easily than fresh bread. It is a popular saying that fresh bread lies heavily in the stomach. However, it has been shown before *in vitro* that in the digestion of bread by diastatic enzymes, fresh bread is most easily digested. Wherein lies the explanation of these apparently conflicting observations? . . . In the case of dogs having an experimental esophageal fistula it was found that salivated and chewed bread crumb has an entirely different consistency than the crumb of stale bread. While in the case of stale bread the mass proved to crumble up very easily, it formed a heavy lump with fresh bread and from this lump small particles break off only with difficulty. Hence, it must be supposed that the movements of the muscles of the stomach readily divide or break up stale bread into small particles, while this is attended with much greater difficulties when fresh bread is involved. In view of this condition the expression that it "lies heavily in the stomach" can be readily understood," p. 117.

After a long controversy between the English scientists, who have been the first to call attention to the considerable part played in the manufacture of beer by the chemical composition of the brewing waters, and the German school that had considered this composition as being indifferent, the influence of the water is nowadays universally admitted and is due, for the greater part, to the reactions between the compounds present in the water and some bodies which accompany starch in the raw material.

"Most of the waters contain alkaline earths, notably calcium, in two forms, the carbonates and the sulphates. The bicarbonate which is formed from the carbonate by the action of carbonic acid constitutes the transitory hardness of the water, as boiling effects a more or less complete precipitation owing to its decomposition. The permanent hardness is produced by the presence of sulphate. It will easily be realized that the predominance of one or the other of these compounds will affect quite differently the composition of the wort, i.e., the result of starch conversion, and that each type of beer requires a special type of brewing water.

"The waters which contain a high amount of calcium carbonate are with reason designated as alkaline waters: their chalk acts as a neutralizer and reduces the acidity of the mash, a fact which, in starch conversion, contributes to diminish the ratio maltose: non-maltose. This statement is in complete agreement with the fact that carbonated waters are *par excellence* adapted for the manufacture of colored beers of the Bavarian type, the characteristic of which is to be relatively poor in alcohol and rich in extract. When no other type of water can be obtained, which is frequently the case, these waters cannot be employed for the production of a pale beer unless they have been previously submitted to a correction treatment capable of eliminating the objectionable carbonate. Among the treatments practised, boiling followed by decantation, or addition of an acid, for instance, sulphuric, may be mentioned, the choice of the procedure to be adopted varying with the different cases," p. 122.

"Furniture veneers are manufactured almost exclusively by the use of alkali starch glues. This creates a tremendous demand for such adhesives and constitutes their most important application. Other classes of wood-working also successfully employ this type of glue, such as the joining of the layers of wood in box shocks, barrel heads, etc. Thousands of tons of the cassava or tapioca starch are imported into America annually for the purpose, as well as to make dextrin adhesives," p. 181.

"The service of a filling, stiffening and adhesive material, and the aid given by a protecting film, applied to white surfaces, suggests the use of a colorless, odorless, low-cost, adhesive material such as starch and we find actually that its use dates back to the inception of both the textile and paper industries. Layers of papyrus were cemented together by starch, and sheets of paper made from rag fibre dipped in starch paste to procure a better writing surface were made many centuries ago. Specimens of these which have been preserved in museums, demonstrate the permanence of starch films by the fact that they today show satisfactory resistance to writing or printer's ink.

"Being applied in a dissolved or wet state, starch functions by forming an adhesive bond between adjacent fibres, thereby adding both stiffness and tensile strength, or between several plies, as when sheets of paper or cloth are combined for the purpose of securing greater strength and rigidity. Starch used as a surface sizing fills voids between fibres, decreases porosity and adds substance. Starch also serves a useful purpose by forming an adhesive surface which tends to hold down projecting surface fibres. If the fabric be dipped in a starch solution and then dried, a film remains on the surface. This film aids materially in several manufacturing processes by resisting abrasion. Continuity of film makes possible truss effects and, therefore, the greatest strength gain. Continuity of film requires a *homogeneous* solution free from undissolved particles. A surface film on a sheet of paper aids in its subsequent use for either printing or writing by keeping the inks on the surface, and thus developing sharper definition of the characters applied. Starch solutions serve also as a viscous *medium* for holding in solution or in suspension colors or pigments so that they may be applied for general surface tinting effects, or so that the colors may be printed on in regular patterns. With evaporation of the solvent, starch functions as the permanent adhesive bonding agent for the colors. Control of solution properties, viscous flow or plasticity, determines the success of these processes," p. 189.

Size is applied to cotton warps in order that they may be woven with a minimum of breakage. When cloth is to be bleached, the size is removed immediately after weaving, p. 215. One particular desizing agent of animal origin is known by the name of Degomma, p. 228.

"Degomma is a creamy powder with a faint meaty odor, and dissolves very readily in water to give a clear or slightly turbid solution. Unlike malt and fungus preparations resembling more the bacterial type of amylase in this respect, Degomma is most active in neutral or slightly alkaline solutions with an optimum pH of about 7.0, although this may vary slightly according to the nature of the buffer salts used in the determination of the strength. The extreme limits of acidity and alkalinity in which this enzyme is still active are pH of 4.0 and pH of 10.0. At these points and beyond the enzyme is not only inactive but actually destroyed.

"The temperature of optimum activity is about 40°C. If used alone, the enzyme is rapidly destroyed above this temperature. However a protecting influence is exerted by certain substances, e.g., common salt or starch, so that in their presence the preparation is quite active at 50°C. Nevertheless at a temperature of 55°C. or higher the enzyme is rapidly destroyed.

"Mention must be made of the enormous effect of certain electrolytes on the amylolytic activity of Degomma. The chief accelerators have been found to be calcium and chlorine ions. In commercial use the bath must contain 0.25 per cent salt and about 40-50 parts per million of lime which corresponds roughly to a soft natural water. If artificially softened water is used then this amount of lime should be added to the water to obtain the maximum effect from the enzyme."

The second part of this first volume is devoted to a classified bibliography which should be of great value. The patent literature is not included as it is proposed to put this in the second volume.

Wilder D. Bancroft

Das Gesetz der chemischen Massenwirkung; seine thermodynamische Begründung und Erweiterung. By Richard Lorenz. 23 X 16 cm; pp. x + 176. Leipzig: Leopold Voss, 1927. Price: 12.50 marks. This is a very interesting book on the mass law. While few people will agree with all the author says, he has a happy way of presenting his subject and nobody can read the book without learning something from it.

The chapters are entitled: the classical form of the mass law; illustrations of the classical mass law; the ideal mass law in its mol-fraction form; the mass law for condensed systems; illustrations for the new form of the mass law; discussions; the transition to the vapor phase; displacements; electromotive forces.

Wenzel may have had a distinct idea of the mass law in 1777 when he wrote that "the strength of the chemical affinity is proportional to the concentration of the reacting substance." The author considers that Richter was the discoverer of the law of chemical proportions (1792), while Dalton was the founder of chemical atomistics. Guldberg and Waage formulated their law (1867) in the words that "the chemical force of substances is proportional to the effective mass, which latter is given by the volume concentration." In 1877 van't Hoff said that "the reaction velocity (not the chemical force) is proportional to the effective mass of the reacting substances." In 1885 van't Hoff "deduced the mass law from the first and second laws of thermodynamics."

In 1873 "the American, Willard Gibbs, the most brilliant of all thermodynamicists and energeticists, began to develop his views on chemical affinity by means of thermodynamics. . . These investigations furnish incontrovertible proof that a treatment of chemical affinity from the thermodynamic view-point not only enables us to give a theoretical foundation for regularities obtained empirically in the field of reaction mechanisms (effects of temperature, pressure, and mass); but also enables us to predict, and even to calculate, an immense number of chemical phenomena, which were not previously known to exist. Among these is the whole field of the phase rule, which latter was discovered theoretically by Gibbs, who had even to invent the nomenclature. Gibbs, was however, so far ahead of his time that he had practically no influence on the development of the mass law. Even now the abstract presentation of Gibbs' papers is so difficult for most chemists that many propositions are worked out thermodynamically, which the author afterwards finds in Gibbs," p. 12.

"We can acclaim van't Hoff as the master of the reversible cycle. No investigator before or after him has been so keen in devising the cycle which is best suited to each particular case." p. 14.

There is no suggestion, p. 39, that the distribution of a solute between two immiscible solvents always increases the miscibility of the two solvents and the point is also not raised whether the concentrations should be volume or mass concentrations. This is the more surprising because, in the very next chapter, he claims for himself the credit, p. 51, of being the first to suggest the use of the mol fraction when dealing with the ideal gas law.

Under vapor pressures for consolute mixtures of two volatile liquids, he says, p. 118, that "one of the two methods of treating this problem starts with the molar thermodynamic potential for condensed phases, making use usually of the van der Waals equation of state. This method started with van der Waals himself and its chief supporter is van Laar. The other line of attack starts from the vapor pressures of the pure components and of the mixtures. It starts with a thermodynamic equation which was deduced by Duhem and by Margules and which has been tested especially by Zawidski. Nernst has also followed a similar path, quite independently. The theory of Dolezalek also falls into this class. The thermodynamic portion is supplemented by a non-thermodynamic assumption, which is not that of an equation of state, as in the first line of attack. It is the assumption of the general validity of the Raoult-van't Hoff law of the lowering of the vapor pressure for all concentrations."

The new form of the mass law, as deduced for two-phase, four-component systems, p. 72, can be written

$$\frac{x}{1-x} - \frac{1-y}{y} = Ke^u,$$

which differs from the old form in that the right hand term is not a constant.

Wilder D. Bancroft

Organic Chemistry. By James Bryant Conant. 22 × 14 cm; pp. xii + 291. New York: The Macmillan Company, 1928. Price: \$2.60. Among other reasons, this book is most interesting because the author has adopted the policy of putting the material into it which a student should be expected to get from it in an introductory course. To this end it is much shorter than most familiar texts.

Many introductory books suffer from excess material which serves to distract the student's attention from the more important points. The description of too many compounds is a particular fault in organic chemistry which undoubtedly tends toward straight memorizing rather than toward obtaining the fundamental concepts of the subject. Excess material may be met with omissions but this is unfortunate since it conveys the impression to the student that he is touching upon more or less miscellaneous points. A good course should not only give him a complete foundation but should emphasize the fact that it is doing so. This new book has been described as "a short concise treatment presenting a minimum of facts and a maximum emphasis on important principles. Not memory work, but independent reasoning and an understanding of method is the objective." This description is accurate and the reviewer is consequently enthusiastic.

Thirty figures illustrating principally important commercial processes, special laboratory set-ups and the variation of physical properties with composition are unusually good and a largely new and commendable feature. Everything is up-to-date. Methyl alcohol from water gas gets more space than methyl alcohol from wood and mercurochrome is described, p. 244. Fortunately this modernity does not prevent the inclusion of numerous historical footnotes. Even more of these would be better since every opportunity should be taken to impress the student with the peculiarly fascinating background of the subject. In this connection one is inclined to miss some reference to Wöhler's synthesis of urea on page 1, although it is given later, p. 97. There are about ten review questions at the end of each chapter.

"The formal classification of compounds which is so valuable to the specialist may be barren to the uninitiated. For this reason, the author has unhesitatingly departed from the traditional arrangement of the subject-matter whenever such departure seemed to promise a more interesting grouping of topics or an easier road to a mastery of the principles of the science," p. v. This is apparent from the list of chapters, as follows: the alcohols; ethers, alkyl halides, esters; petroleum; unsaturated hydrocarbons; rubber; organic acids; esters; fats, oils, and soaps; derivatives of ammonia: amides, amines, urea; aldehydes and ketones; the synthesis of organic compounds; the polyhalogen compounds, methods of determining the structure of complicated organic substances; dibasic acids and hydroxy acids; stereoisomerism; the carbohydrates; malonic ester and acetoacetic ester; the hydrocarbons from coal tar; aryl halides and phenols; aromatic nitro compounds and amines; aminophenols and polyhydroxy compounds; the diazonium salts and the azo dyes; aromatic acids; aliphatic compounds with aryl groups; natural and synthetic dyes and drugs; the proteins.

"The author's experience in presenting organic chemistry to a variety of classes has led him to believe that the alcohols have certain advantages over the hydrocarbons as a point of departure. The necessity for structural formulas can be convincingly demonstrated by the consideration of the isomerism of ethyl alcohol and methyl ether, and attention can be centered on a relatively few accessible compounds with characteristic reactions. From many points of view the relationship of alcohol and ether to water is much more important than the relationship of these substances to ethane," p. v. There is undoubtedly room for opinion on this point, and the reviewer is inclined to favor the standard way. Petroleum compares very favorably with the alcohols in the matter of beginning with familiar material. Further it seems better to start with the direct combination of hydrogen and carbon to form methane and lead from this to the synthesis of the oxygen compounds than to give the student alcohol and ether directly. Their names are probably familiar but the initial plunge into their chemistry seems liable to worry him more than the direct combination of two elements. The question is most interesting but not vital. Organic chemistry can be introduced satisfactorily either way.

The reviewer is particularly pleased with the following: the synthesis of organic compounds, pp. 117-125; methods of determining structure, pp. 130-135; the directive influence of substituents, pp. 194-196; aromatic syntheses, pp. 226-227; aliphatic compounds with aryl groups, pp. 248-257. The author has indeed succeeded in his attempt "to present an interesting and at the same time adequate account of the compounds of carbon.

Robert L. Nugent

An Account of the Principles of Measurement and Calculation. By Norman Robert Campbell. 22 x 14 cm; pp. ix + 293. London: Longmans, Green and Company, Price: 12 shilling, 6 pence. The author complains that the principles of measurement and calculation are neglected, even if they are occasionally understood, and since he is of the opinion that there is much to be said about measurement in general which is not to be found in any of the usual text-books or treatises and which is yet intrinsically interesting, illuminating to the student, and useful to the experimental and theoretical physicist in the practice of their science," he has set himself the task of supplying the deficiency. The book opens with a very abstract treatment of the meaning of numerical laws, then deals with the theory of measurement, with "dimensions" and with the theory of errors, in which the method of least squares and the error function of Gauss are characterised as "based on a theory which I believe to be completely false and dangerously misleading." The treatment may, therefore, be expected to diverge in some respects from the usual ones.

The book is difficult to follow: the highly abstract character of much of it (in spite of Dr. Campbell's frequent assertion of the contrary) is made still less tangible by the free use of abbreviations which are not tabulated or indexed. The following is a fair specimen of much of the text. "Two systems that balance the same combination of numbers of the S. S. may not balance each other and the differences in their real magnitudes may be $> E_m$;

the margin of uncertainty concerning the real magnitude of any system not a member of the S. S. is still $> E_m$ but $< 2E_m$. And the uncertainty can hardly be removed by making every system we want to measure a member of the S.S. and subjecting it to the process of adjustment; for if we add a new member to the S.S., we must add also other members sufficient to maintain or increase $k-m$."

Dr. Campbell's book is thoughtfully and sincerely written, and its study will benefit all who have occasion to make measurements and then try to interpret them. It is clearly based on the experience of an able laboratory worker extending over a long period, combined with a keen desire to understand the fundamental meaning of such activity. Although it will be found difficult by most physical chemists, who are not accustomed to the rather abstract type of argument so frequently used, they will discover in it many directly practical suggestions, and some theoretical discussions, such as those on the dimensions of physical magnitudes, which are stimulating and provoke thought. It is to be regretted that the author has not included in this section some account of the very ingenious "ultimate rational units" of Professor G. N. Lewis.

The equation of adiabatic expansion on p. 90 is incorrect, and the equation on p. 159, line 7, should, apparently, read $P = p_1 p_2 \dots$

J. R. Partington

Einführung in die Chemie in leichtfasslicher Form. By Lassar-Cohn. Seventh edition. Edited by M. Mechling. 28 × 16 cm; pp. vi + 247. Leipzig: Leopold Voss, 1927. In view of the discussion which is now going on in the United States as to the proper place in which to introduce the metals in a course on general chemistry, it is interesting to note that Lassar-Cohn, who has been very successful with his books, brings the metals in on pp. 192-231, at the very end of the book.

With all due respect to the author and to his experience, the reviewer believes that this is certainly wrong in a popular book and probably wrong in a general course. The boy is familiar with electrodeposited gold, silver, and nickel, to which chromium plate must now be added. He knows aluminum, zinc, iron, lead, tin, copper, mercury, and platinum. He is familiar with magnesium through flash-lights and with tungsten through incandescent lamps. He certainly knows brass, bronze, and solder, and he has possibly heard of duralumin and monel metal. As against this he has no first-hand knowledge of chlorine, bromine, or fluorine, though he may have had tincture of iodine put on his ankle. He has ordinarily no knowledge of the acids or of the alkalies outside of ammonia. He may have seen sulphur and he has heard of arsenious oxide under the name of arsenic. He does not know anything about phosphorus, except a reference to matches and to phosphorescence; and salt means sodium chloride to him, very properly. In spite of all this, nearly everybody takes up metals last. Baker at Syracuse does not; but his example is not yet being followed to any great extent.

The book is well written and has the obvious advantage of giving what the public thinks it wants. It does not present the subject in the proper way and cannot, therefore, be the last word. It is a great pity that the author apparently never considered the question of order of presentation of the topics.

Wilder D. Bancroft

Physikalisch-chemische Übungen. By W. A. Roth. Fourth edition. 22 × 16 cm; pp. viii + 316. Leipzig: J. A. Barth, 1928. Price: 18 marks, bound 15 marks. After a general introduction the author takes up: densities; molecular weights in solution, thermochemistry, optical constants; chemical statics and dynamics; electrical conductance; Faraday's law; potential differences; electrostatics; colloid chemistry.

Under colloid chemistry the sub-heads are: Brownian movements; Tyndall phenomenon; ultra microscope; preparation of colloidal solutions; electrical transference of colloids; coagulation; adsorption; ultra-filtration; catalysis; with five supplementary pages on surface tension and viscosity.

Wilder D. Bancroft

35-537

ELECTRICAL CONDUCTION IN TEXTILES. I

The Dependence of the Resistivity* of Cotton, Silk and Wool on Relative Humidity and Moisture Content

BY E. J. MURPHY AND A. C. WALKER

It is a well-known fact that textiles are very hygroscopic and that the resistance of a textile insulating material is very largely governed by the humidity of the air to which it is exposed. In 1914 S. Evershed¹ made an extensive investigation of the effect of moisture on the insulation resistance of a number of insulating materials, including cotton, from which he concluded that electrical leakage in such materials is practically entirely due to moisture condensed on their external and internal surfaces. More recently quantitative relationships between insulation resistance and relative humidity have been determined for cotton, silk and other fibrous insulating materials by Kujirai and Akahari.² Measurements of the conductance of individual cotton fibers as a function of relative humidity have been made by Slater.³ His results show that in the range 40-80% relative humidity the logarithm of the conductance of the fibers is a linear function of relative humidity. In none of this work, however, does it appear to have been shown whether the relationship between resistance and relative humidity is chiefly an attribute of the fibrous structure⁴ of textiles or of some more fundamental structure such as that of cellulose in the case of cotton. An attempt to answer this question is one of the objects of the present investigation.

The present paper contains a discussion of data obtained in a study of the resistance-humidity and resistance-moisture content relationships for cotton, silk and wool. To determine the significance of these relationships the textiles were studied in different forms, namely, as single fibers, as short threads, and as the covering of standard insulated wires. The effect of electrolytic impurities in the textile was also determined. Factors affecting the accuracy of the measurements on textiles are discussed. Other phases of the general problem of conduction in textiles will be considered in subsequent papers.

Briefly, the results indicate that the insulation resistance of a textile sample is determined by its moisture content in such a way that if the logarithm of the resistance is plotted against the logarithm of the moisture content a

* While the data given in this paper are for the insulation resistance of sample of these textiles, it has been found that the insulation resistance of these samples does not differ significantly from their resistance and is proportional to the resistivity of the material.

¹ S. Evershed: *J. Inst. El. Eng. (London)*, 52, 51 (1914).

² Kujirai and Akahari: *Sci. Papers, Inst. Phys. Chem. Res. (Tokyo)*, 1, 94 (1923).

³ F. P. Slater: *Proc. Roy. Soc.*, 96B, 181 (1924).

⁴ The conductance of a textile might be due chiefly to moisture adsorbed on the surfaces of the fibers or condensed in the interstices between them. H. L. Curtis (*Bur. of Standards, Bull.*, 11, 359 (1914-15)) has shown that the surface resistivity of a large number of materials is very sensitive to changes in relative humidity.

straight line is obtained whose slope is independent of the form of sample and of the amount of impurities contained in the textile, but is characteristic of the kind of material tested, i.e., whether silk, wool, or cotton. That the resistance at a given relative humidity is also dependent on the amount of impurities indicates that the conduction takes place largely through water paths whose conductivity is dependent on the concentration of electrolytic matter. If these water-paths are pictured as forming a regular space-pattern, the elements of which change in dimensions with the moisture content in a way characteristic of the textile, the observed relationships may readily be explained.

Description of Materials Studied

The samples used in this investigation are listed below with a brief description of the form in which they were tested.

1. Cotton Threads I.—Ash content, 1.0%. Size of thread, 30/2. Number of threads in parallel, 2000.
2. Cotton Threads II.—Ash content, 0.26%.¹ Size of thread, 40/2. Number of threads in parallel, 1600.
3. Twisted Pairs² I.—Ash content about the same as Sample I. Kind of wire, No. 18 double cotton covered tinned copper. Number of twisted pairs in parallel, 36.
4. Twisted Pairs³ II.—Ash content about the same as Sample 2. Number of twisted pairs in parallel, 15.
5. Silk Threads I. (Tussah)—Ash content, 2.1%. Size of thread, 62/16. Number of threads in parallel, 360.
6. Silk Threads⁴ II.—Ash content, 0.28%. Size of thread, 62/16. Number of threads in parallel, 240.
7. Wool Threads.—White darning wool. Number of threads in parallel, 100.
8. Single Cotton Fibers.—Ash content, 1.07%. Number of fibers in parallel, 60.

These samples were chosen so as to differ from each other in form, in dimensions, and in ash content, and therefore provide data regarding the influence of these factors on their electrical characteristics. Since the ash is largely composed of electrolytes, samples of relatively low ash content have also a relatively low electrolyte content.

¹ Although this cotton was obtained commercially, it is probable that it was washed during manufacturing operations, so that the water-soluble constituents of the ash were largely removed.

² See description of experimental methods.

³ The insulated wire from which this sample was made was of the same stock as Sample 3, but was washed in boiling water for 30 minutes to reduce the amount of impurities.

⁴ This silk is from a lot of cultivated silk which was washed to reduce the water-soluble content.

Experimental Method

The above described samples were prepared for test in the following three ways:

Fibers.—The single fibers were pulled out of a thread of cotton with tweezers and mounted by means of a very thin glue solution on electrodes consisting of two concentric brass rings of 1.3 cm. difference in radius, supported on a well-insulated hard-rubber panel. It was necessary to mount 60 or more fibers in parallel to produce adequate galvanometer deflections for resistance measurements at low humidities.

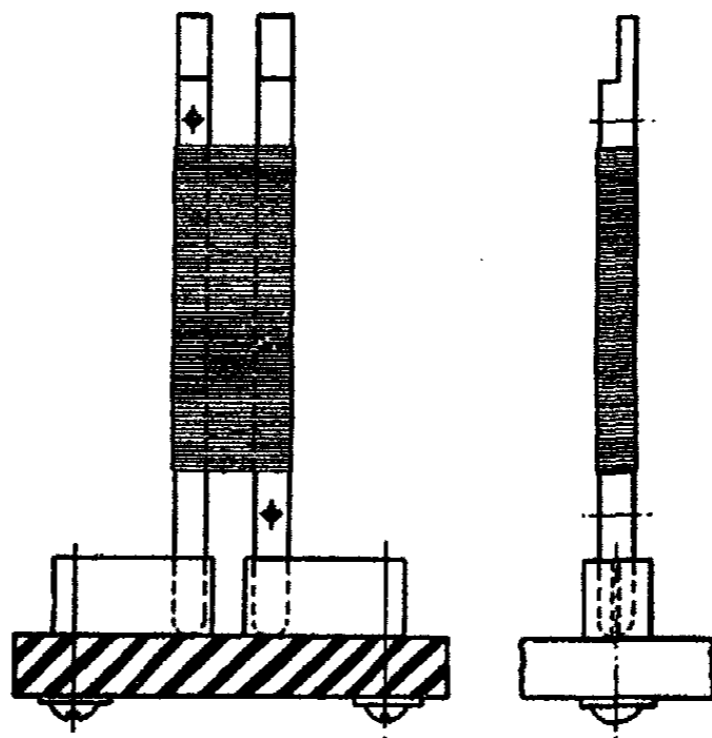
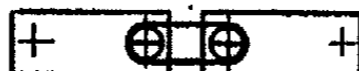


FIG. 1

The Electrode-Fixture for measuring the Resistance of Threads

Threads.—The samples for making electrical measurements on threads were prepared by winding 30 to 100 turns of a continuous length of thread around two brass posts¹ 1.3 cm. apart between centers (Fig. 1). Several units of this kind were mounted on a well-insulated hard-rubber panel and connected in parallel, forming a sample consisting of a large number of threads in parallel,² the separation of the electrodes being 1.3 cm. (e.g., sample 1 consisted of 2000 threads in parallel each 1.3 cm. in length.)

¹ The threads were held in place and in contact with the posts only by their own tension. Preliminary experiments were also made with posts fitted with bars by which the threads were clamped tightly to the posts to ensure good electrical contact. It was found that both types of posts served equally well as electrodes, the contact resistance at the electrodes being less than 5%, so the simpler type was adopted.

² There was a distinct advantage in having a large number of threads in parallel both at very low and at very high humidities. The measurements could be extended to lower humidities than would have been possible with a smaller number of threads, and at high humidities could be made with a milliammeter instead of a galvanometer, thus reducing the error due to polarization. Reducing the length of the threads is not as desirable as increasing their number for it makes polarization and other secondary effects more prominent.

"*Twisted Pairs.*"—This form of sample was chosen in order to simulate the conditions under which a textile is used in service, and consisted simply of two cotton insulated wires twisted together. No. 22 double cotton covered copper wire was used. Preliminary trials showed that by putting eight twists in a length of 5 cm., twisted pairs were obtained which were closely reproducible in insulation resistance and other electrical characteristics as well as convenient in size. The method of twisting may be understood by reference to Fig. 2. The two ends of a piece of No. 22 cotton insulated copper wire

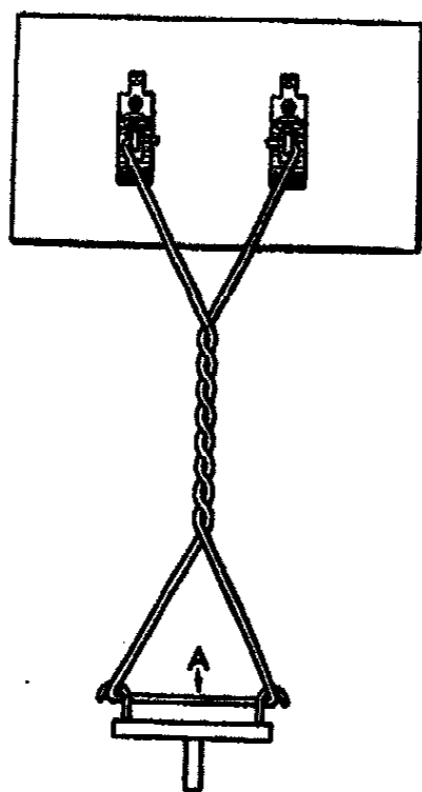


FIG. 2

Diagram showing Method of preparing Twisted Pairs

38 cm. long were fastened in two clips mounted 5 cm. apart, and a metal rod weighing about 2 kgm. was suspended from this loop of wire by means of two hooks also 5 cm. apart. The weight of the rod provided a constant tension during the twisting operation, which consisted simply in rotating the rod several times about its vertical axis. After cutting the wire at A, the sample consisted essentially of two copper conductors insulated from each other by four layers of cotton, two layers on each wire. Several samples of this kind were mounted on a hard rubber panel and connected in parallel to facilitate the measurement of the resistance of the sample at low humidities.

For all types of samples the electrodes were mounted on hard rubber panels which formed the lids of glass crystallizing dishes, or "humidifiers" (22 cm. diameter, 11 cm. deep), in which were put the sulphuric acid solutions used to produce the desired relative humidities. The electrodes

were on the under side of the lids and electrical connection was made to them from outside the humidifier by means of the screws by which they were attached to the lids. To reduce surface leakage over the hard rubber to a minimum it was covered with ozokerite, a wax of very low surface conductivity. The ozokerite was applied by melting it and pouring over the surfaces across which leakage might occur. When so prepared no detectable surface leakage took place between the electrodes except when exposed to relative humidities greater than about 99.5%, where the leakage was still negligible. The humidifiers containing the samples were placed in an air-chamber maintained at constant temperature to within $\pm 0.5^\circ\text{C}$; the air-chamber was itself immersed in a water bath whose temperature was kept constant to $\pm 0.1^\circ\text{C}$. The arrangement of the air-chamber was such that the leads necessary to make electrical connection to the samples were attached only while measurements were actually being made and a sufficiently long section of the leads was inside the chamber so that heat conduction to the samples during a measurement, due to the difference between the temperature of the room and the air-chamber, was negligible.

The relative humidities to which the samples were successively exposed were produced by sulphuric acid solutions.¹ The specific gravities of these solutions and the relative humidities which they produced, as obtained from Wilson's relative humidity-specific gravity curves,² are given in Table I. The samples were exposed to these humidities for 18 hours, after which time the rate of change of resistance with time is very slow and the samples could be regarded as substantially at equilibrium.

TABLE I

| Specific Gravity | Relative Humidity % | Specific Gravity | Relative Humidity % |
|------------------|---------------------|------------------|---------------------|
| 1.5465 | 10.0 | 1.2200 | 75.5 |
| 1.4785 | 19.5 | 1.1988 | 79.1 |
| 1.4275 | 30.0 | 1.1590 | 85.2 |
| 1.3820 | 38.8 | 1.1395 | 88.4 |
| 1.3297 | 50.5 | 1.1345 | 89.0 |
| 1.2924 | 59.0 | 1.1080 | 92.0 |
| 1.2412 | 70.8 | 1.0642 | 96.3 |
| 1.2293 | 73.0 | 1.0300 | 98.6 |

The resistance of the samples varied from 20 ohms to about 10^{13} ohms depending on the humidity and type of sample. Because the range of resistance was so large four different methods of measurement were used, each better adapted for a particular range than the others. A few of the measurements at humidities lower than 10% were made by a leakage method, the circuit for which is shown in Fig. 3A. The capacity C was charged through the sample R and then discharged through the galvanometer. The resistance of the sample is given by

$$R = \frac{E t}{K_1 \theta}$$

where R is in ohms, t the number of seconds for which the voltage E was applied, θ the ballistic throw obtained on discharging the condenser, and K_1 is the ballistic sensitivity of the galvanometer in coulombs/mm., determined by charging the condenser to known voltages and discharging it through the galvanometer. The voltage to which the condenser C was charged by the leakage current was small as compared with the applied voltage. For humidities between 10 and 80% a direct deflection method was used (Fig. 3B). The resistance of the sample is given by

$$R = \frac{E}{K_2 D} - S,$$

where D is the galvanometer deflection in mm., S a standard megohm (usually negligible in comparison with the first term), and K_2 the current sensitivity

¹ Saturated salt solutions were also used to produce various relative humidities with results which agreed substantially with those obtained with sulphuric acid solutions; but all of the humidities used in the data reported here were produced with the sulphuric acid solutions listed in Table I.

² R. E. Wilson: J. Ind. Eng. Chem., 13, 326 (1921).

in amperes/mm., determined by applying known voltages when the circuit contained only the standard megohm and the galvanometer. The calibrating voltages (provided by a potential divider) were chosen so that the calibration points corresponded within a millimeter with the scale deflections observed in the measurements and a calibration was made after each measurement for the scale deflection observed in that measurement. A sensitive

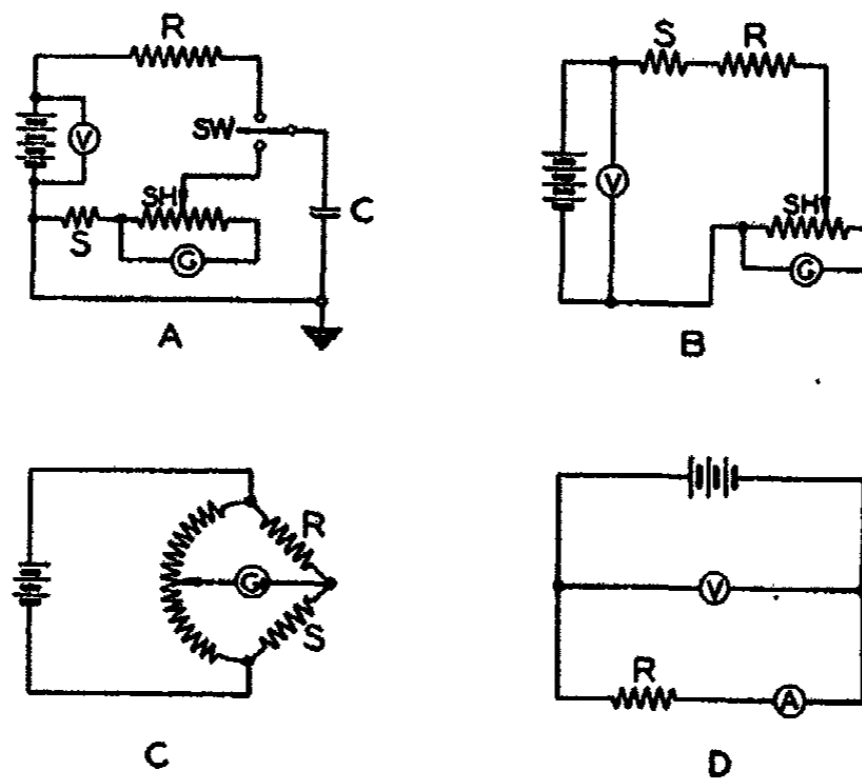


FIG. 3

Electrical Circuits for the Measurement of Insulation Resistance.

A—Leakage Method; B—Direct Deflection Method; C—Ohmmeter Method; D—Voltmeter-Milliammeter Method.

R—textile sample, G—high sensitivity galvanometer, G₁—pointer type galvanometer, S—standard resistance, C—air condenser, SH—Ayrton shunt, SW—discharging switch.

galvanometer is unsuitable for measurements at humidities above 80-85% because an appreciable increase in the resistance of the sample is caused by the measuring current during the 30 seconds to 1 minute required to obtain a reading. It was found that in the range 80-95% measurements could be made with sufficient rapidity with a Leeds and Northrup Ohmmeter to avoid error due to this cause. This instrument is a Wheatstone bridge with a single calibrated dial by means of which a measurement can be made in a few seconds (Fig. 3C). The resistance of the sample is given by $R = K_3 S$, where S is a standard resistance and K_3 a calibration factor. At humidities above 95% the current through the samples was large enough to measure with a milliammeter, and the circuit shown in Fig. 3D was used. This had the advantage that a milliammeter reading could be obtained by an application of the measuring voltage for a second or so, and the resistance changes

which occurred in this time were usually negligible.¹ The resistance is given by $R = (E/I) - A$, where I is the current in amperes and A the resistance of the milliammeter.

Precision of Measurements

The possible error in these methods of measurement due to insensitivity and errors of calibration is estimated to be less than $\pm 1\%$ under the most favorable conditions and about $\pm 5\%$ under unfavorable conditions. It was frequently possible to use two or even three of these methods to measure the same resistance. The agreement of the different methods is illustrated by Table II. This is a good indication that there are no systematic errors of

TABLE II

| Sample and Conditions | Resistance (megohms) | |
|-----------------------------------|-----------------------|-----------------------|
| Cotton Threads I, at 10% R. H. | by direct deflection, | 2.49×10^6 |
| | by leakage, | 2.47×10^6 |
| Cotton Threads II, at 10% R. H. | by direct deflection | 2.0×10^7 |
| | by leakage, | 1.98×10^7 |
| Cotton Threads II, at 96.3% R. H. | by direct deflection, | 0.59 |
| | by ohmmeter, | 0.59 |
| Cotton Threads II, at 89% R. H. | by direct deflection, | 6.6 |
| | by ohmmeter, | 6.5 |
| Cotton Threads II, at 85.2% R. H. | by direct deflection, | 1.39×10 |
| | by ohmmeter, | 1.3×10 |
| Cotton Threads I, at 76.1% R. H. | by direct deflection, | 1.88 |
| | by ohmmeter, | 1.86 |
| Cotton Threads I, at 96.3% R. H. | by ohmmeter, | 1.06×10^{-2} |
| | by milliammeter | 1.15×10^{-2} |

appreciable amount in the methods of measuring resistance, for the four methods involved the use of different apparatus and the measurement of several different quantities such as time, capacity and voltage in the leakage method, current and voltage in the direct deflection and milliammeter methods, and the ratio of two resistances in the Ohmmeter method.

The factor which causes the greatest difficulty in making precise measurements on textiles at humidities greater than about 80% is the increase in resistance with time of application of the measuring current, called hereafter "polarization." By using rapid methods of measurement when necessary the

¹ At very high humidities the initial reading of the milliammeter was sometimes in doubt on account of the rapidity of decrease of the current. In these cases a second measurement was made with the current flowing in the opposite direction. In the second measurement the current increased with time for a second or so and approached closely to the initial value. The measurements were also confirmed by repeating them after the samples had been allowed about 30 minutes to recover from the previous measuring current. The rapid changes of resistance which take place at very high humidities are not always evident when a galvanometer of long period is used.

error in the present data due to this cause was reduced to less than 5% on the average, but at humidities very close to 100% the error may be as large as 20%. Comparison of the present results with preliminary measurements in which no measures were taken to avoid polarization shows that at humidities near 100% an error by as much as a factor of 50 in the resistance might be caused by neglecting the effect of polarization. At humidities below about 10% the resistance of samples of small electrode separation also increases with time with sufficient rapidity to cause an error which may be as large as 20%, but only two or three measurements were made under these conditions.

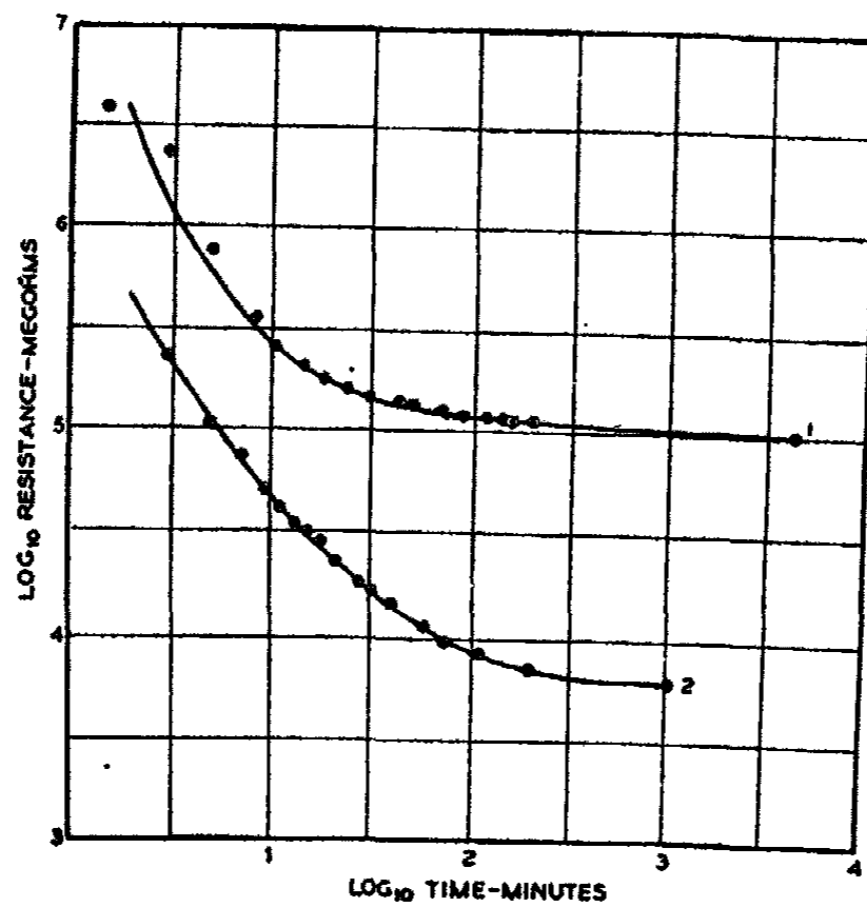


FIG. 4

Change of Resistance of Cotton Threads with Time of Exposure to 76% Relative Humidity at 25°C.

1. A sample of low electrolyte content.
2. A sample of normal electrolyte content.

Resistances are for a single 1.3 cm. length of thread.

Other possible sources of error in the measurements are: failure of the samples to reach equilibrium at a given humidity, uncertainty in the humidity corresponding to a given specific gravity of the sulphuric acid solutions, and fluctuations in temperature. The samples used in the present work were small and a large surface was exposed to the air relative to their volume; in the case of the thread samples it seems probable that the inner fibers were exposed to air of about the same humidity as the outer ones. This probably favored the rapid attainment of equilibrium. The rate of approach to equilibrium is illustrated by Fig. 4, which shows that after 100 to 200 minutes the rate of change is very slow. A period of 18 hours for equilibrium was adopted as a standard procedure. Tests made to determine how much further change

in resistance would take place in several days showed an average change of less than 6% and a maximum change of 14%.

The relative humidity corresponding to a given specific gravity could be read to $\pm 2\%$; the percentage error corresponding to this deviation varies from $\pm 2\%$ at 10% relative humidity to $\pm 2\%$ at 100% relative humidity. The specific gravities of the solutions were the same within the experimental error at the end of the investigation as at the beginning.

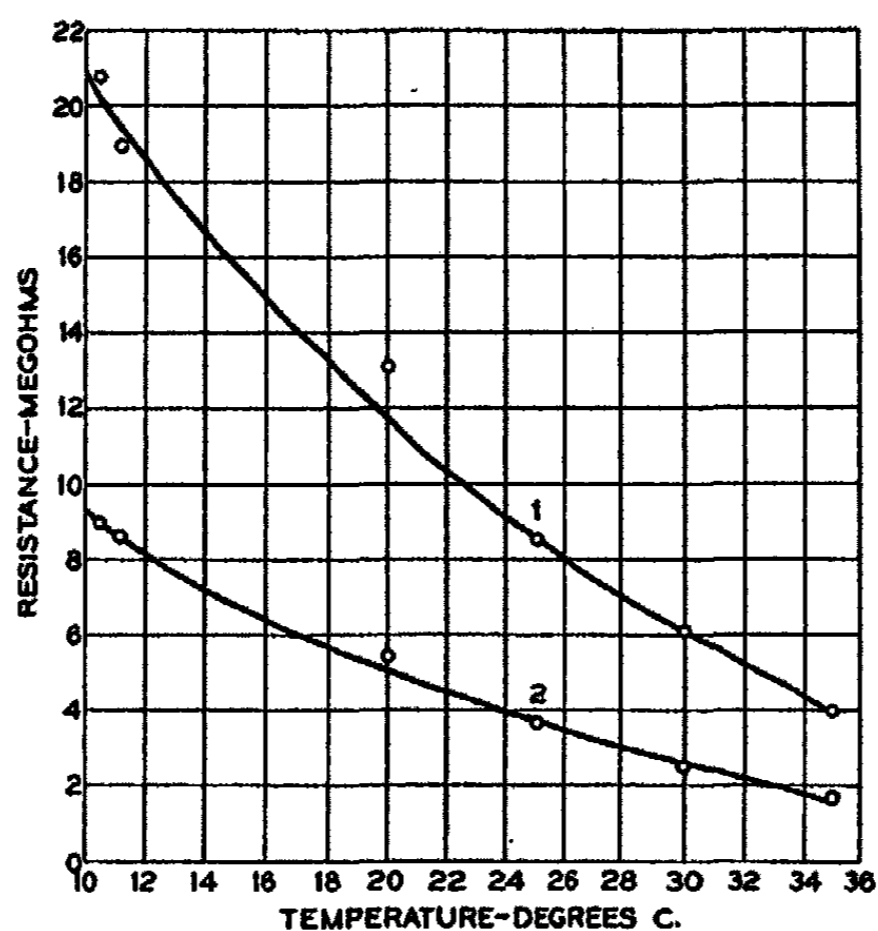


FIG. 5

Change of Insulation Resistance of Cotton Samples with Temperature at 76% Relative Humidity.

Curve 1 is the insulation resistance ($\times 10^{-4}$) of a sample of low electrolyte content.

Curve 2 is the insulation resistance ($\times 10^{-3}$) of a sample of normal electrolyte content. The data are given in Table III.

It was found that the resistance of cotton samples decreases by about 8% per degree at 25°C. Typical data are plotted in Fig. 5. Since the humidifiers were kept at a temperature constant to $\pm 0.5^\circ\text{C}$ the error due to fluctuations in temperature is probably $\pm 4\%$.

From the above analysis it is estimated that the error in the data for the resistance of a given sample under given conditions of humidity, temperature, etc. is not greater than $\pm 20\%$ and on the average less than $\pm 10\%$, with the exception of the data in Table VII which were obtained without adequate temperature control. In the plots of the resistance and relative humidity data, the circles indicate approximately the estimated accuracy with which the points have been determined, although they are not intended strictly as precision circles. This does not apply to the resistance-moisture content

data, for the error in the moisture content was larger than that in the relative humidity for reasons which will be given later. The errors in the data for silk and wool are of the same order of magnitude as in those for cotton. It will be evident from the data which follow that these errors are small as compared with the change in resistance produced by a small change in relative humidity.

Experimental Data and Discussion

The present investigation was preceded by a study of the properties of textiles at a single fixed humidity in which it was found that the variation of resistance from one sample to another of the same material is small enough that textiles could be regarded as having, in effect, a reasonably well-defined resistivity. Because of the rather irregular dimensions of cotton fibers and the possibility that the resistance of a cotton thread, for example, would be very sensitive to small changes in tension or other uncontrollable factors, it was not obvious that this would be the case. However, the results of measurements of the resistance of several hundred single cotton fibers (measured in groups of 60 in parallel), of several thousand short cotton threads (in groups of 50 in parallel) and of a large number of twisted pairs show that the variation of resistance from sample to sample is considerably less on the average than the change in the resistance of a given sample produced by a small change in humidity (1 or 2%). The samples were representative of a considerable supply of cotton and its resistivity was practically unchanged over a period of two or three years. The resistance of cotton threads was found to be insensitive to small changes in tension. Silk shows a similar uniformity of effective resistivity. It was also found that the resistance of a cotton thread containing n fibers is $1/n$ th of the average resistance of the fibers of which it is composed, and that the resistance of a thread is proportional to its length (at least up to 8 cm.). From consideration of such facts as these we have concluded that the resistance¹ of a cotton or silk sample of any form is propor-

TABLE III

Variation of Insulation Resistance with Temperature

The data are for the resistance of a single No. 30/2 cotton thread 1.3 cm. long exposed to a relative humidity of 76%. Sample 1 has a low electrolyte content; sample 2 the normal electrolyte content.

| Temp. °C | Resistance (megohms) | | Temp. °C | Resistance (megohms) | |
|-------------|----------------------|--------------------|-------------|----------------------|--------------------|
| | Sample 1 | Sample 2 | | Sample 1 | Sample 2 |
| 10.6 | 2.08×10^6 | 9.05×10^5 | 25.0 | 8.56×10^4 | 3.70×10^3 |
| 11.2 | 1.90 | 8.70 | 30.0 | 6.14 | 2.55 |
| 20.0 | 1.31 | 5.46 | 35.0 | 3.98 | 1.75 |

¹The quantity measured in the present investigation was the "insulation resistance." This is the effective resistance between electrodes and includes the resistance of the contact between the textile and the electrodes and may also be partly due to a back-emf of polarization. In a later paper it will be shown, however, that the resistance of the contact between the textile and the electrodes is negligible, that the effect of the back-emf of polarization is also negligible except possibly in one or two measurements on twisted pairs at humidities lower than 10%, and that the resistance of a cotton thread is uniformly distributed along its length under the conditions of the present measurements. There is therefore no distinction between the insulation resistance of the samples and their resistance in the present data.

TABLE IV

Insulation Resistance vs. Relative Humidity and Moisture Content for Cotton at 25° C

H is the relative humidity in percent, M_a and M_d the moisture content in percent of the dry weight for "absorption" and "desorption" respectively, and R is the resistance in megohms of a single thread 1.3 cm. long or a single twisted pair.

| Cotton Threads I | | | Cotton Threads II | | |
|------------------|-------|----------------------|-------------------|-------|----------------------|
| H | M_a | R | H | M_a | R |
| 6.0 | 1.62 | $3.28 \cdot 10^{10}$ | 30.0 | 3.69 | $1.39 \cdot 10^9$ |
| 10.0 | 2.00 | $5.68 \cdot 10^9$ | 38.8 | 4.41 | $2.83 \cdot 10^8$ |
| 19.5 | 2.82 | $4.46 \cdot 10^8$ | 50.5 | 5.38 | $3.05 \cdot 10^7$ |
| 30.0 | 3.69 | $4.74 \cdot 10^7$ | 59.0 | 6.17 | $6.70 \cdot 10^6$ |
| 38.8 | 4.41 | $8.09 \cdot 10^6$ | 73.0 | 7.98 | $4.40 \cdot 10^5$ |
| 50.5 | 5.38 | $8.62 \cdot 10^5$ | 79.1 | 9.04 | $1.38 \cdot 10^5$ |
| 59.0 | 6.17 | $1.62 \cdot 10^5$ | 89.0 | 11.89 | $1.37 \cdot 10^4$ |
| 70.8 | 7.66 | $1.72 \cdot 10^4$ | 98.6 | 19.28 | $5.47 \cdot 10^2$ |
| 73.0 | 7.98 | $1.15 \cdot 10^4$ | | M_d | |
| 75.5 | 8.41 | $6.73 \cdot 10^3$ | 89.0 | 14.29 | $9.42 \cdot 10^3$ |
| 79.1 | 9.04 | $3.28 \cdot 10^3$ | 88.4 | 14.13 | $1.15 \cdot 10^4$ |
| 85.2 | 10.60 | $6.40 \cdot 10^2$ | 79.1 | 11.35 | $7.43 \cdot 10^4$ |
| 88.4 | 11.56 | $2.76 \cdot 10^2$ | 73.0 | 10.00 | $1.90 \cdot 10^6$ |
| 92.0 | 13.19 | $9.90 \cdot 10$ | 59.0 | 7.76 | $2.17 \cdot 10^6$ |
| 96.3 | 16.40 | $2.30 \cdot 10$ | 50.5 | 6.70 | $1.02 \cdot 10^7$ |
| 98.6 | 19.28 | 3.94 | 38.8 | 5.37 | $9.50 \cdot 10^7$ |
| | M_d | | 30.0 | 4.47 | $2.60 \cdot 10^8$ |
| 98.6 | 19.28 | 5.48 | 19.5 | 3.47 | $1.47 \cdot 10^9$ |
| 96.3 | 17.78 | $1.63 \cdot 10$ | 10.0 | 2.46 | $4.12 \cdot 10^{10}$ |
| 92.0 | 15.48 | $4.27 \cdot 10$ | | | |
| 88.4 | 14.13 | $1.01 \cdot 10^2$ | Twisted Pairs II | | |
| 85.2 | 13.03 | $1.55 \cdot 10^2$ | H | M_a | R |
| 79.1 | 11.35 | $4.44 \cdot 10^2$ | 19.5 | 2.82 | $8.48 \cdot 10^6$ |
| 75.5 | 10.52 | $1.51 \cdot 10^3$ | 30.0 | 3.69 | $1.26 \cdot 10^6$ |
| 73.0 | 10.00 | $1.96 \cdot 10^3$ | 38.8 | 4.41 | $2.31 \cdot 10^5$ |
| 70.8 | 9.59 | $2.30 \cdot 10^3$ | 50.5 | 5.38 | $2.45 \cdot 10^4$ |
| 59.0 | 7.76 | $1.56 \cdot 10^4$ | 59.0 | 6.17 | $5.75 \cdot 10^3$ |
| 50.5 | 6.70 | $6.03 \cdot 10^4$ | 73.0 | 7.98 | $2.86 \cdot 10^2$ |
| 38.8 | 5.37 | $4.62 \cdot 10^6$ | 79.1 | 9.04 | $7.95 \cdot 10$ |
| 30.0 | 4.47 | $3.72 \cdot 10^6$ | 89.0 | 11.89 | 6.15 |
| 19.5 | 3.47 | $3.14 \cdot 10^7$ | | M_d | |
| 10.0 | 2.46 | $2.92 \cdot 10^8$ | 79.1 | 11.35 | $2.05 \cdot 10$ |
| 6.0 | 1.88 | $4.96 \cdot 10^9$ | 73.0 | 10.00 | $7.56 \cdot 10$ |
| 2.0 | 1.00 | $3.32 \cdot 10^{11}$ | 59.0 | 7.76 | $1.11 \cdot 10^3$ |

TABLE IV (continued)

| Twisted Pairs I | | | 50.5 | 6.70 | $6.53 \cdot 10^3$ |
|-----------------|-------|----------------------|------|-------|----------------------|
| | M_a | | 98.6 | 19.28 | $9.00 \cdot 10^{-2}$ |
| 2.0 | 1.00 | $4.07 \cdot 10^7$ | 96.3 | 17.78 | $2.64 \cdot 10^{-1}$ |
| 10.0 | 2.00 | $2.20 \cdot 10^8$ | 92.0 | 15.48 | 1.17 |
| 19.5 | 2.82 | $2.04 \cdot 10^8$ | 89.0 | 14.29 | 2.70 |
| 30.0 | 3.69 | $2.10 \cdot 10^8$ | 85.2 | 13.03 | 7.50 |
| 50.5 | 5.38 | $3.80 \cdot 10^2$ | 79.1 | 11.35 | $1.84 \cdot 10$ |
| 59.0 | 6.17 | $7.57 \cdot 10$ | 73.0 | 10.00 | $8.70 \cdot 10$ |
| 70.8 | 7.66 | 6.42 | 70.8 | 9.59 | $1.35 \cdot 10^2$ |
| 73.0 | 7.98 | 4.22 | 59.0 | 7.76 | $1.36 \cdot 10^3$ |
| 75.5 | 8.41 | 2.82 | 50.5 | 6.70 | $4.54 \cdot 10^3$ |
| 79.1 | 9.04 | 1.27 | 38.8 | 5.37 | $4.07 \cdot 10^4$ |
| 85.2 | 10.60 | $2.44 \cdot 10^{-1}$ | 30.0 | 4.47 | $1.93 \cdot 10^6$ |
| 88.4 | 11.56 | $1.02 \cdot 10^{-1}$ | 19.5 | 3.47 | $1.72 \cdot 10^6$ |
| 92.0 | 13.19 | $3.54 \cdot 10^{-2}$ | 10.0 | 2.46 | $1.86 \cdot 10^7$ |
| 96.3 | 16.40 | $6.36 \cdot 10^{-3}$ | | | |
| 98.6 | 19.28 | $1.52 \cdot 10^{-3}$ | | | |

1. These resistances were measured with an applied voltage of 100.

2. The moisture content data were obtained from Urquhart and Williams' (J. Text. Inst., 15, T438 (1924)) data for soda-boiled cotton at 25°C. Their data for "absorption" are used to give the moisture content corresponding to resistances measured in the ascending order of relative humidities and their data for "desorption" for resistances measured in the descending order of relative humidities.

tional to the resistivity of the textile of which it is composed under the given conditions.

The insulation resistances of the cotton, silk and wool samples which have been described above were measured over a large range of relative humidity at 25°C. In the first series of measurements each successive measurement was made at a relative humidity higher than the preceding one (the "ascending series"); the measurements were then repeated at the same relative humidities but in the reverse order, each measurement being made at a relative humidity lower than the preceding one (the "descending series"). The complete data for both sets of measurements on cotton are given in Table IV.¹ In order to show the main relations between the curves for the different samples without the complication introduced by the fact that the curves for the ascending and descending series are not coincident but form a "hysteresis loop," the data for the ascending series alone will be discussed first.

In Fig. 6 the logarithms of the insulation resistances of four cotton samples, Cotton Threads I and II and Twisted Pairs I and II, are plotted against relative humidity from the data in Table IV for the ascending series. It is to be noted: (i) that in the range 20 to 80% relative humidity the curves are straight lines and (ii) that, in spite of marked differences in their form and ash content, these samples give curves which are parallel to each other within the experimental error.

¹ With the exception of data obtained with measuring voltages other than 100.

Similar data for single cotton fibers are plotted separately in Fig. 7; the curve for Cotton Threads I is repeated in Fig. 7 as Curve E to facilitate the comparison of single fibers with threads and twisted pairs. Curves A, B and C are plotted from Slater's data.¹ Since his conductance data are expressed in arbitrary units the position of these curves relative to the other curves in Fig. 7 is also arbitrary. Curve D is plotted from Table V, which contains

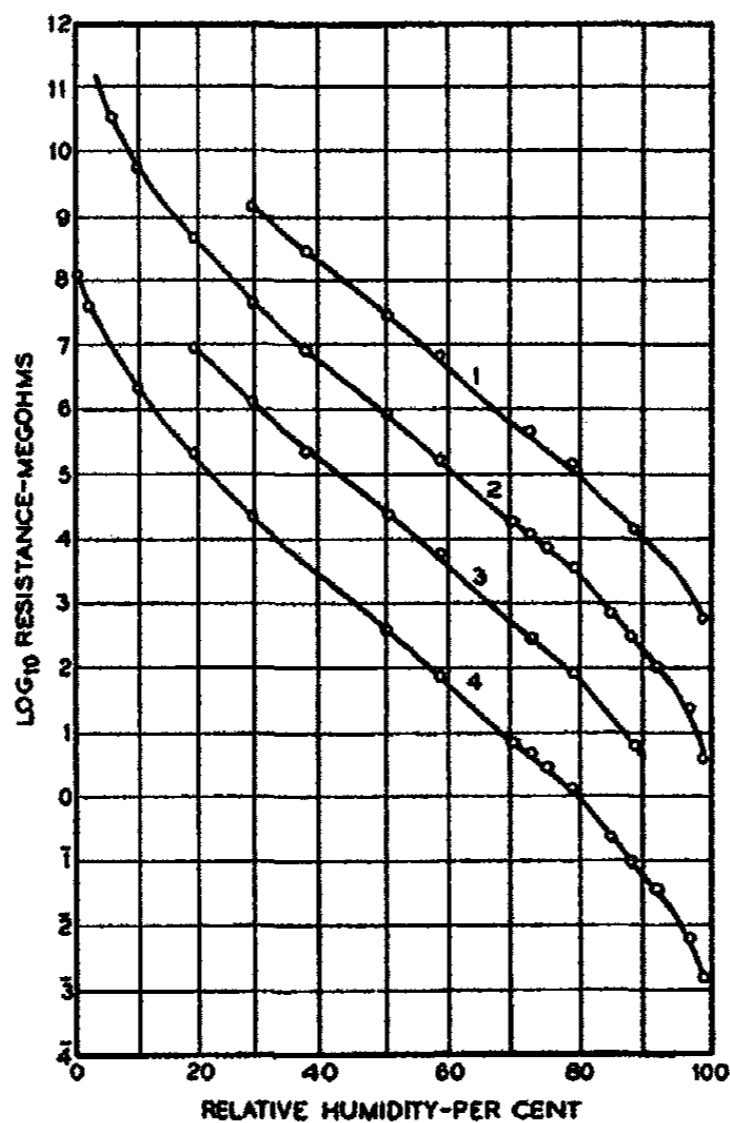


FIG. 6

Insulation Resistance of Cotton Threads and Twisted Pairs as a Function of Relative Humidity.

1. Cotton Threads II
2. Cotton Threads I
3. Twisted Pairs II
4. Twisted Pairs I

The resistances are for a single 1.3 cm. length of thread or for a single twisted pair.

TABLE V

Insulation Resistance of Single Cotton Fibers at Room Temperature: Length of Fibers, 1.3 cm.

| Relative Humidity % | Resistance Megohms | Relative Humidity % | Resistance Megohms |
|---------------------|--------------------|---------------------|--------------------|
| 37 | 2.37×10^8 | 77 | 3.75×10^6 |
| 75 | 5.62×10^5 | 96 | 1.0×10^4 |

¹ Loc. cit.

data obtained by a few rather inaccurate measurements of the resistance of single cotton fibers, made before adequate temperature control was available. A comparison of these curves shows that over a considerable range of relative humidities Slater's curves for single cotton fibers are straight lines approximately parallel to our curves for cotton threads and twisted pairs. Within its very wide limits of error Curve D is also approximately parallel to Curve

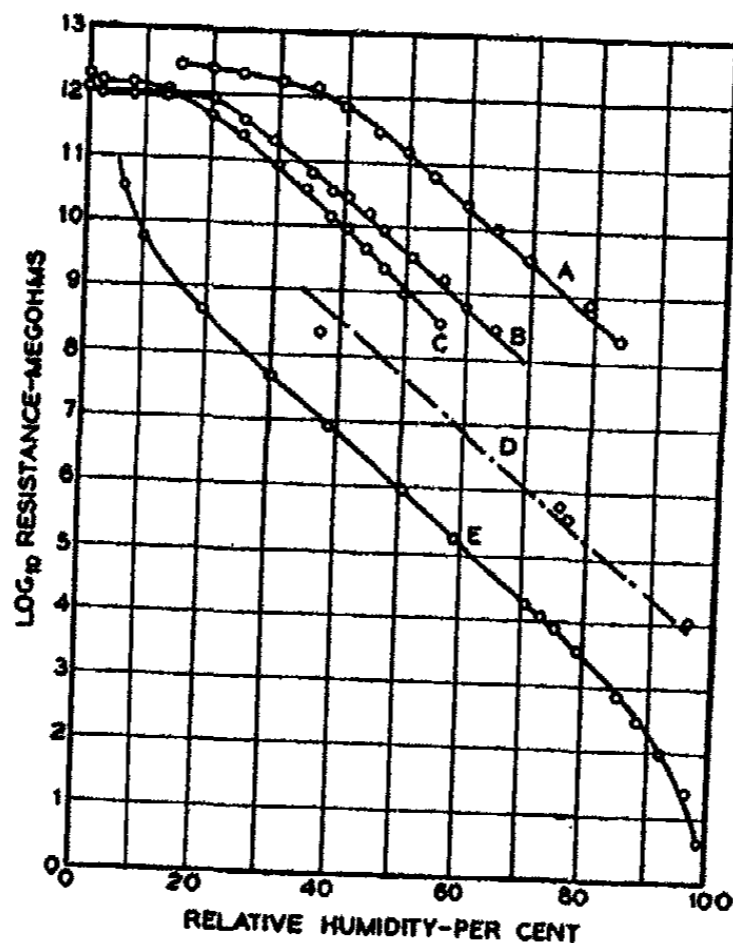


FIG. 7

Insulation Resistance of Single Cotton Fibers as a Function of Relative Humidity.

A, B and C are Slater's Specimens A, B and C.

D is plotted from Table V.

E is Curve 2 of Fig. 6 repeated.

E. That the resistance of single cotton fibers becomes almost independent of humidity for low humidities, as indicated by Slater's curves, is probably not real, but due to the conductance of the insulating supports of the fiber becoming of the same order of magnitude as that of the fiber itself.

From the resistance-humidity relations shown by Figs. 6 and 7 the following conclusions may be drawn: (i) in the range 20 to 80% the insulation resistance of cotton threads, twisted pairs and single fibers is an exponential function of relative humidity which can be expressed logarithmically by the following equation:

$$\text{Log } R = -8.5 \times 10^{-2} H + A,$$

where R is the resistance of the sample in megohms, H the relative humidity in percent, and A a constant which has a value of 7.0 for Twisted Pairs I, 8.6 for Twisted Pairs II, 10.2 for Cotton Threads I, 11.7 for Cotton Threads II, and 11.9 for Single Fibers; (ii) since the curves for samples differing from

each other as widely as these are identical in form within the experimental error, it is very probable that this form of curve is characteristic of cotton, and that such factors as the form, dimensions, and ash or electrolyte content of the particular sample determine only the positions of the individual curves.

As stated earlier, the value of insulation resistance obtained for a given relative humidity is somewhat dependent on whether the sample has been previously exposed to a higher or lower relative humidity. In Figs. 6 and 7

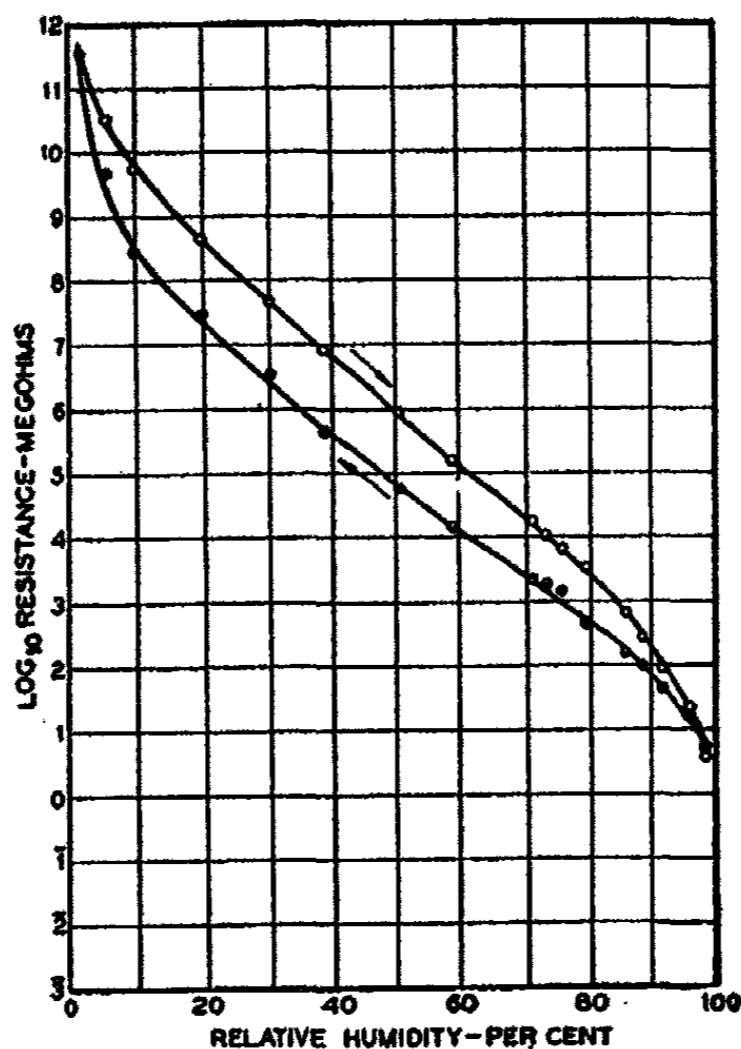


FIG. 8

Insulation Resistance-Relative Humidity Curve for Cotton Threads I Showing the Dependence of Insulation Resistance on the Direction from which Equilibrium is approached. The resistances are for a single 1.3 cm. length of thread.

only the data obtained by measurements made in the order of increasing relative humidity were plotted. When, in addition, the data for measurements made in the order of decreasing relative humidities are plotted, a "hysteresis loop" such as that shown in Fig. 8 is obtained. At the widest part of this loop the resistance corresponding to a given relative humidity on the ascending branch of the curve is over ten times as great as that corresponding to the same relative humidity on the descending branch. The loop closes at its lower end at about 2% relative humidity and at its upper end at about 96%. There is a slight difference in the slopes of the descending and ascending branches of the logarithm of resistance vs. relative humidity curves, the descending branch having a slightly smaller slope than the ascending.

Approximately this same difference in slope has been observed in other measurements both on twisted pairs and on threads. This indicates that as long as all measurements are made either as an ascending or a descending series, the curves for the logarithm of resistance vs. relative humidity will be parallel regardless of the form of the samples or their ash content.

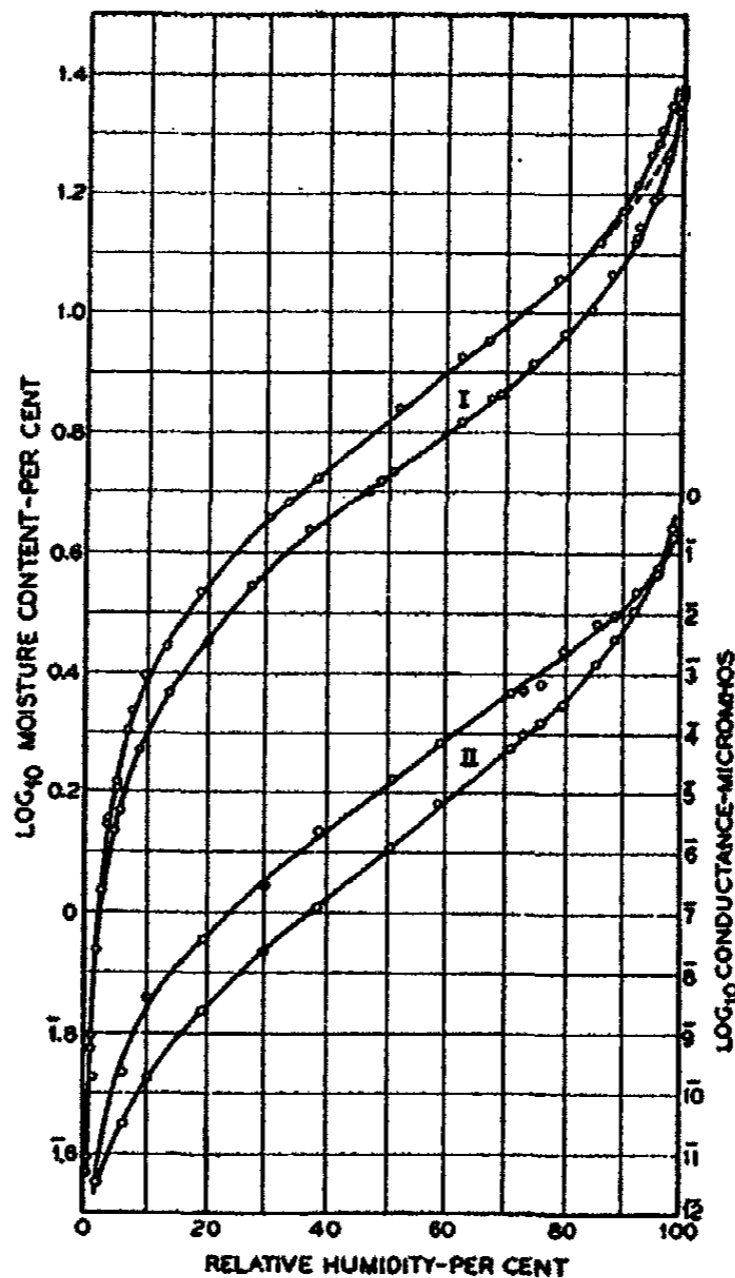


FIG. 9

- I. Moisture Content of Cotton as a Function of Relative Humidity at 25°C.
- II. Reciprocal of Insulation Resistance of Cotton Threads I as a Function of Relative Humidity.

The moisture content is in percent of the dry weight. The conductances are for a single 1.3 cm. length of thread.

In Fig. 9 the logarithm of the moisture content of cotton is plotted against relative humidity, using Urquhart and Williams' data.¹ This curve is similar in form to the curve for the logarithm of resistance vs. relative humidity. This is more evident when the reciprocal of resistance is plotted instead of the resistance, as has been done for Cotton Threads I in Fig. 9. Both curves have similar inflections and a hysteresis loop. By comparing the moisture content corresponding to any given conductance on the ascending curve with

¹ J. Text. Inst., 15, T438 (1924) (Table I).

that corresponding to the same conductance on the descending curve it is found that a given conductance on either curve corresponds to approximately the same moisture content. This suggests that the resistance of a cotton sample is determined by its moisture content irrespective of the relative humidity with which it is in equilibrium.

In view of the simplicity of the relation between resistance and moisture content suggested by these facts, the resistance data which were plotted in Figs. 6 and 8 as a function of relative humidity have been plotted in Fig. 10

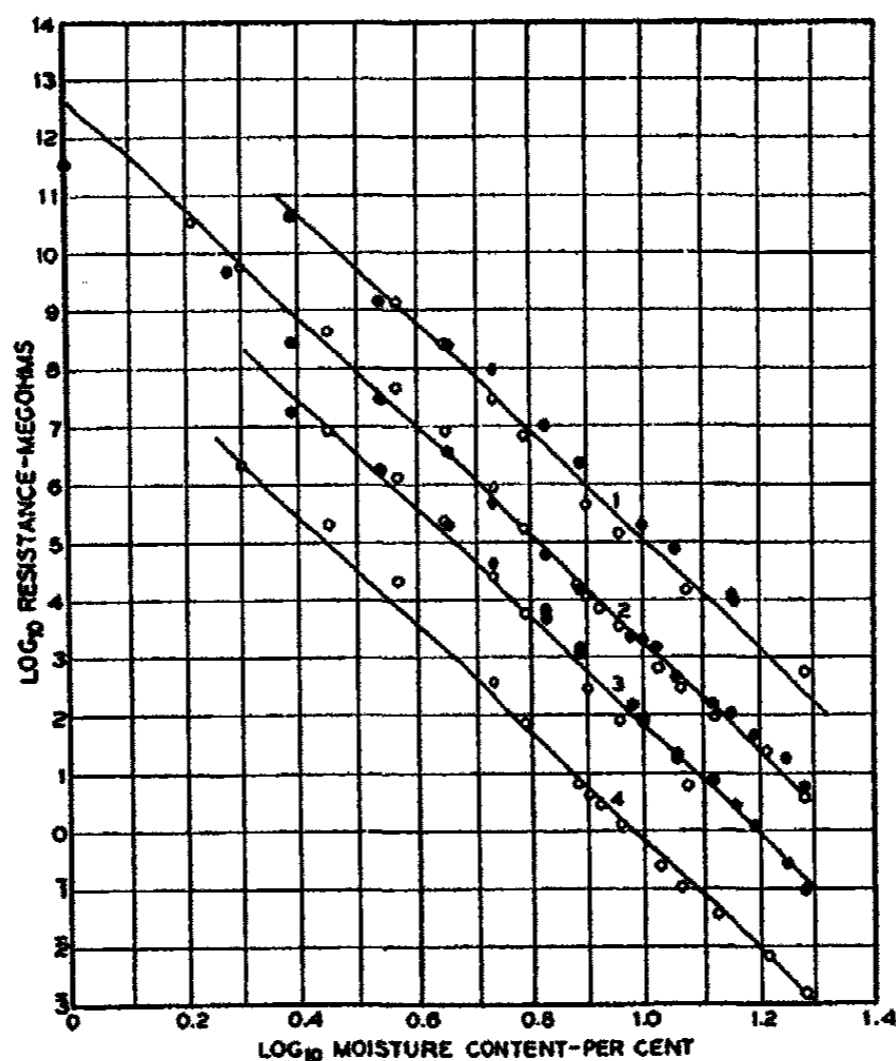


FIG. 10

Insulation Resistance of Cotton as a Function of Moisture Content.

- | | |
|----------------------|---------------------|
| 1. Cotton Threads II | 3. Twisted Pairs II |
| 2. Cotton Threads I | 4. Twisted Pairs I |

○ Ascending order of humidities.
● Descending order of humidities.

The resistances are for a single 1.3 cm. length of thread or for a single twisted pair.

as a function of moisture content. It is evident that there are no inflections in these curves corresponding to those shown in Fig. 6, and that the data can be best represented by straight lines. Such departures as do occur are undoubtedly due to the inapplicability of the moisture content data of Urquhart and Williams to the samples used in the resistance measurements. These investigators have shown that the hygroscopicity of cotton varies with its source and treatment.¹ Not only were the types of cotton on which the

¹ J. Text. Inst., 15, T143 (1924); 17, T39 (1926).

moisture content determinations were made different from those on which the resistance measurements were made, but also a longer time was allowed for equilibrium at each humidity in determining the moisture content than in measuring the resistance. These differences in samples and procedure would appear from Urquhart and Williams' work to be sufficient to explain the deviations from the straight lines.

For Curves 1, 2 and 3 the resistances measured in the ascending order of relative humidities are plotted against Urquhart and Williams' moisture content data for "absorption" and the resistances measured in the descending order against their data¹ for "desorption". These curves show that when resistance is plotted against moisture content there is no hysteresis loop corresponding to that which appears when the same data are plotted against relative humidity as in Fig. 8. The fact that Curves 2 and 4 are parallel shows that the slope of the resistance-moisture content curve is independent of the form of the sample, since twisted pairs and threads are very dissimilar in form. Also since Curves 1 and 3 are parallel to Curves 2 and 4, the slope is independent of the ash or electrolyte content of the samples.

The following equation fits the curves of Fig. 10 and therefore expresses the resistance of these samples over practically the whole range of moisture contents (i.e., 1% to 22.4%):

$$\log R = -9.3 \log M + B,$$

where R is the resistance of the sample in megohms, M the moisture content in percent of the dry weight, and B a constant having the value 9.1 for Twisted Pairs I, 11.2 for Twisted Pairs II, 12.6 for Cotton Threads I, and 14.4 for Cotton Threads II. The above equation can also be written, $R = B' M^{-9.3}$, where $B = \log B'$. The quantitative relations expressed by this equation may be illustrated by the fact that by halving the moisture content, independent of its original value, the resistance of any cotton insulation is increased by a factor of about 600. Reducing the moisture content from 22.4% to 1%, or the humidity from 98.6 to 2%, increases the resistance by a factor of about 10^{12} . To give a numerical measure of the agreement of this equation with the data, the moisture content corresponding to a given relative humidity has been calculated by substituting the observed resistance corresponding to that humidity in the equation and solving for M . The values so obtained are tabulated in Table VI along with the moisture contents obtained directly from the moisture content-relative humidity data. The average deviation is only 3.5%. Since the moisture content data were not obtained under exactly the same conditions as the resistance data, this agreement is as good as could be expected.

These results point directly to the conclusion that the moisture content of the cotton, and not the prevailing relative humidity, is the controlling

¹ In making the resistance measurements the highest humidity to which the samples were exposed was 98.6%, while the cycle of humidities used by Urquhart and Williams in determining the moisture content included 100% relative humidity. To correct for this difference the curve shown in dotted lines in Fig. 9 was used to obtain the logarithm of moisture content for relative humidities above 88%. This correction makes no change in the position of the curve.

factor in determining its resistance, i.e., the only significant effect of a change in relative humidity is the change which it produces in the moisture content of the cotton. Hence by making a single measurement of resistance and moisture content on a given sample of cotton, the resistance at any other moisture content (or the humidity corresponding to it either for increasing or decreasing humidities) may be calculated with considerable accuracy.

TABLE VI

Comparison of Moisture Contents calculated from Observed Resistances with those given by the Moisture Content—Relative Humidity Data

| H | R | M _{cal} | M _{obs} | ΔM | ΔM% |
|------|-------------------------|------------------|------------------|-------|-------|
| 6.0 | 3.28 · 10 ¹⁰ | 1.67 | 1.62 | -0.05 | -3.1 |
| 10.0 | 5.68 · 10 ⁹ | 2.02 | 2.00 | -0.02 | -1.0 |
| 19.5 | 4.46 · 10 ⁸ | 2.66 | 2.82 | +0.16 | +6.0 |
| 30.0 | 4.74 · 10 ⁷ | 3.39 | 3.69 | +0.30 | +8.8 |
| 38.8 | 8.09 · 10 ⁶ | 4.10 | 4.41 | +0.31 | +7.6 |
| 50.5 | 8.62 · 10 ⁵ | 5.19 | 5.38 | +0.19 | +3.7 |
| 59.0 | 1.62 · 10 ⁵ | 6.24 | 6.17 | -0.07 | -1.1 |
| 70.8 | 1.72 · 10 ⁴ | 7.94 | 7.66 | -0.28 | -3.7 |
| 73.0 | 1.15 · 10 ⁴ | 8.26 | 7.98 | -0.28 | -3.5 |
| 75.5 | 6.73 · 10 ³ | 8.79 | 8.41 | -0.38 | -4.5 |
| 79.1 | 3.28 · 10 ³ | 9.48 | 9.04 | -0.44 | -4.9 |
| 85.2 | 6.40 · 10 ² | 11.30 | 10.60 | -0.70 | -6.6 |
| 88.4 | 2.76 · 10 ² | 12.36 | 11.56 | -0.80 | -6.9 |
| 92.0 | 9.90 · 10 | 13.49 | 13.19 | -0.30 | -2.2 |
| 96.3 | 2.30 · 10 | 16.22 | 16.40 | +0.18 | +1.1 |
| 98.6 | 3.94 | 19.59 | 19.28 | -0.31 | -1.6 |
| 98.6 | 5.48 | 18.88 | 19.28 | +0.40 | +2.1 |
| 96.3 | 1.63 · 10 | 16.83 | 17.78 | +0.95 | +5.6 |
| 92.0 | 4.27 · 10 | 15.07 | 15.48 | +0.41 | +2.7 |
| 88.4 | 1.01 · 10 ² | 13.80 | 14.13 | +0.33 | +2.4 |
| 85.2 | 1.55 · 10 ² | 13.15 | 13.03 | -0.12 | -0.9 |
| 79.1 | 4.44 · 10 ² | 11.80 | 11.35 | -0.45 | -3.8 |
| 75.5 | 1.51 · 10 ³ | 10.28 | 10.52 | +0.24 | +2.3 |
| 73.0 | 1.96 · 10 ³ | 10.00 | 10.00 | 0.00 | 0.0 |
| 70.8 | 2.30 · 10 ³ | 9.84 | 9.59 | -0.25 | -2.5 |
| 59.0 | 1.56 · 10 ⁴ | 8.02 | 7.76 | -0.26 | -3.2 |
| 50.5 | 6.03 · 10 ⁴ | 6.92 | 6.70 | -0.22 | -3.2 |
| 38.8 | 4.62 · 10 ⁵ | 5.57 | 5.37 | -0.20 | -3.6 |
| 30.0 | 3.72 · 10 ⁶ | 4.45 | 4.47 | +0.02 | +0.4 |
| 19.5 | 3.14 · 10 ⁷ | 3.54 | 3.47 | -0.07 | -2.0 |
| 10.0 | 2.92 · 10 ⁸ | 2.79 | 2.46 | -0.33 | -11.8 |
| 6.0 | 4.96 · 10 ⁹ | 2.06 | 1.88 | -0.18 | -8.8 |
| 2.0 | 3.32 · 10 ¹¹ | 1.31 | 1.00 | -0.31 | -31.0 |

Average percentage deviation = 3.54% (omitting 31 and 11.8).

In order to explain the significance of the data just presented we may assume that cotton is a complex system of cellulose, water and impurities in definite ratios. Then the relationships shown by the resistance-humidity and resistance-moisture content curves for twisted pairs, threads and single fibers indicate that this complex system may be regarded as having a definite specific resistance which is determined by the values of the ratios of its constituents. This implies that the total resistance of a textile is not appreciably affected by the resistances of the contacts between the fibers of which it is composed or by the arrangement of the fibers relative to the direction of current flow.

Further support for this conclusion has been obtained from the results of a large number of measurements of the resistance of single cotton fibers and of threads of the same material at a fixed humidity. These data have shown that the resistance of a single fiber is n times that of a thread containing n fibers in its cross-section. It has also been found that the resistance of a cotton thread increases in direct proportion to its length, even for lengths greater than that of any single fiber. This would not be expected if contact resistances between fibers formed a significant part of the total resistance.

The discussion so far has been confined to the results of measurements made on cotton. Similar data were also obtained for silk and wool but for a smaller humidity range. These data are given in Tables VII and VIII. From the relations shown by cottons of different electrolyte content it would be

TABLE VII
The Insulation Resistance of Silk Threads as a Function of Humidity and Moisture Content

| H | M | Silk Threads I (Tussah) | | Silk Threads II | |
|------|-------|----------------------------|---|-------------------|-------------------|
| | | R | R | Sample 1 R | Sample 2 R |
| 38.8 | 7.57 | $1.60 \cdot 10^8$ | | | |
| 50.5 | 8.77 | $2.24 \cdot 10^7$ | | | $1.09 \cdot 10^9$ |
| 59.0 | 9.91 | $6.37 \cdot 10^6$ | | | $4.15 \cdot 10^8$ |
| 70.8 | 11.89 | $2.32 \cdot 10^5$ | | | $2.86 \cdot 10^7$ |
| 73.0 | 12.36 | $1.38 \cdot 10^5$ | | $1.41 \cdot 10^7$ | $1.96 \cdot 10^7$ |
| 75.5 | 12.91 | $8.82 \cdot 10^4$ | | $5.65 \cdot 10^6$ | $1.39 \cdot 10^7$ |
| 79.1 | 13.77 | $8.57 \cdot 10^3$ | | $2.02 \cdot 10^6$ | $1.64 \cdot 10^6$ |
| 85.2 | 15.78 | $5.58 \cdot 10^2$ | | $1.73 \cdot 10^5$ | $1.01 \cdot 10^5$ |
| 88.4 | 17.10 | $1.69 \cdot 10^2$ | | $6.15 \cdot 10^4$ | $3.50 \cdot 10^4$ |
| 92.0 | 19.28 | $7.06 \cdot 10$ | | $6.87 \cdot 10^3$ | $6.60 \cdot 10^3$ |
| 96.3 | 23.99 | 8.10 | | $6.60 \cdot 10^2$ | $6.53 \cdot 10^2$ |
| 98.6 | | 2.37 | | $1.90 \cdot 10^2$ | $2.16 \cdot 10^2$ |

H is the relative humidity in percent.

M the moisture content of the silk in percent of the dry weight based on Schloesing's data.

R is the insulation resistance of a single 1.3 cm. length of thread measured with an applied voltage of 100.

TABLE VIII
Insulation Resistance of Wool Yarn at 25° C

| H | M | R | H | M | R |
|------|-------|-------------------|------|-------|-------------------|
| 50.5 | 12.97 | $7.53 \cdot 10^7$ | 85.2 | 20.51 | $2.96 \cdot 10^4$ |
| 59.0 | 14.22 | $2.26 \cdot 10^7$ | 88.4 | 22.28 | $1.15 \cdot 10^4$ |
| 70.8 | 16.18 | $2.21 \cdot 10^6$ | 92.0 | 24.83 | $2.03 \cdot 10^3$ |
| 73.0 | 16.67 | $1.35 \cdot 10^6$ | 96.3 | 30.06 | $1.78 \cdot 10^2$ |
| 75.5 | 17.26 | $6.97 \cdot 10^5$ | 98.6 | | $3.10 \cdot 10$ |
| 79.1 | 18.20 | $2.40 \cdot 10^5$ | | | |

H is the relative humidity in percent.

M is the moisture content of the wool in percent.

R the resistance of a single 1.3 cm. length of yarn.

Applied voltage 100.

expected by analogy that the curve for Silk Threads II would lie above that for Silk Threads I and be parallel to it since Silk Threads II have a lower electrolyte content than Silk Threads I. The curves in Fig. 11 show that in this respect cotton and silk behave alike.

In Fig. 12 the resistance data have been plotted as a function of moisture content. The logarithm of resistance vs. logarithm of moisture content curves are straight lines within the error in the moisture content data as applied to these samples. The moisture content data were taken from a paper by Schloesing.¹ His experimentally determined values for unbleached raw China silk and for wool at 24°C were recalculated to 25°C, using temperature coefficients based on his data. While only four points are given in the range 36% to 96% humidity for the moisture content of this type of silk, these data are supported by similar measurements on three other kinds of silk. The deviations of the points from the lines in Fig. 12 are of the order of magnitude to be expected from the small but appreciable variations in the hygroscopicity of silk with its source and treatment, as also shown by Schloesing's data, and from the long interpolations necessitated by the small number of points.

In our judgment the following equations best fit the curves for silk and wool and therefore express the insulation resistances of these samples as functions of their moisture contents:

For silk,

$$\begin{aligned} \log R &= -16.0 \log M + C, \text{ or} \\ R &= C' M^{-16.0}, \end{aligned}$$

where R is the resistance in megohms of a single silk thread 1.3 cm. long, M the moisture content of the silk in percent of its dry weight, and C (= log C') a constant which has the value 22.4 for Silk Threads I, and 24.5 for Silk Threads II;

¹ Th. Schloesing: Bull. soc. encour. indust. nat., 8, 717 (1893); Comptes rend., 116, 808 (1893); Text. World Record (Boston), Nov., p. 219 (1908).

For wool,

$$\begin{aligned} \log R &= -16.4 \log M + D, \text{ or} \\ R &= D' M^{-16.4}, \end{aligned}$$

where R is the resistance in megohms of a single 1.3 cm. length of wool yarn, M the moisture content of the wool, and $D = \log D' = 26.0$. From the values of the exponents of M , it is evident that silk and wool are even more sensitive to changes in moisture content than is cotton since the resistance of silk increases by a factor of about 65,000, and that of wool by one of about 90,000, when their moisture contents are halved, whereas the factor for cotton is 600 or approximately 1/100 that for silk and 1/150 that for wool.

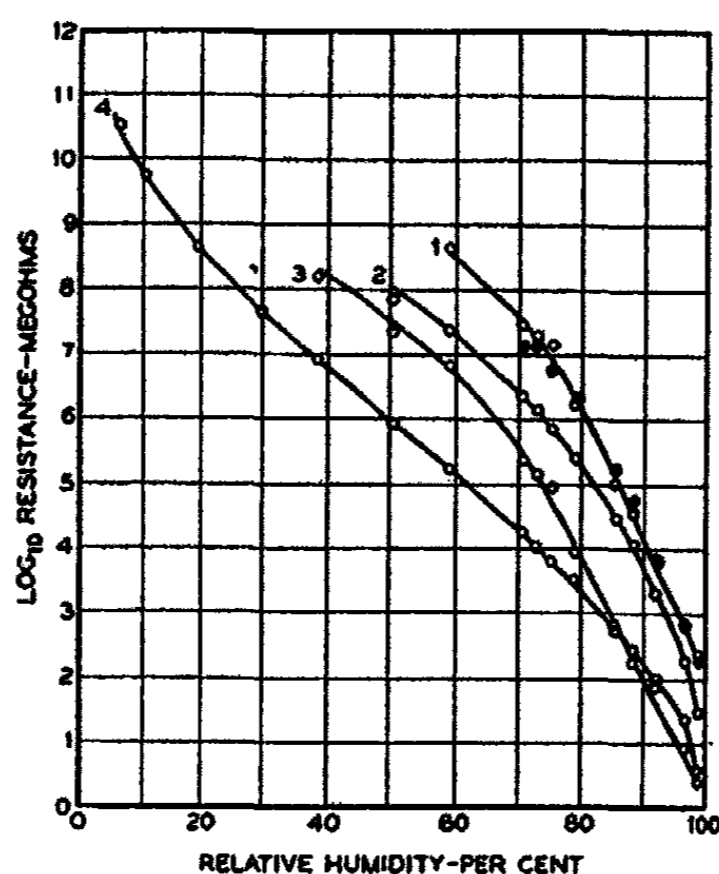


FIG. 11

Insulation Resistance as a Function of Relative Humidity for Wool, Silk and Cotton.

1. Silk Threads II (○ Sample 1, ● Sample 2)
2. Wool Yarn
3. Silk Threads I
4. Cotton Threads I

The resistances are for a single 1.3 cm. length of thread or for a single twisted pair.

The curves in Fig. 11 afford a comparison of the relative insulating qualities of cotton, silk and wool for humidities greater than 40 or 50%. Comparison with the moisture content-humidity curves in Figs. 9 and 13 shows that the greater the hygroscopicity of the textile the greater the resistance of similar samples of the raw textile, which is directly contrary to what would be expected in view of the dependence of the conductivity of a textile on its moisture content. However, this unexpected result can be readily explained by the relations shown in Fig. 12 from which it is evident that a given quantity of moisture distributed in cotton has a higher conductance than the same quantity of moisture in silk, and that a similar relation holds between silk

and wool though the difference is smaller. These relations appear reasonable if, for example, we assume for textiles any model in which the conducting water-paths form a regular network or space-pattern which corresponds to some regularity in the structure of the textile (e.g., in the structure of cellulose), the form or dimensions of the elements of the network being different for different textiles. Then the conduction paths in any direction may be considered to consist effectually of elementary filaments of water containing

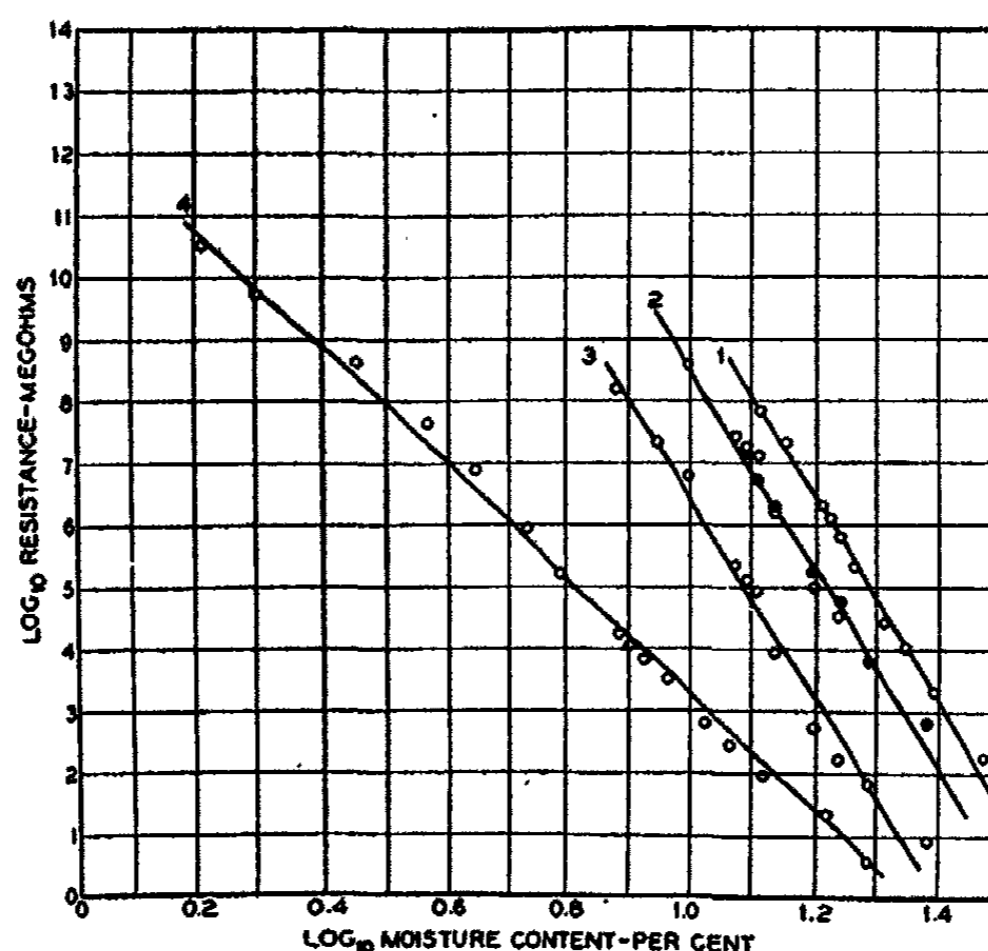


FIG. 12

Insulation Resistance as a Function of Moisture Content for Wool, Silk and Cotton.

1. Wool Yarn
2. Silk Threads II (○ Sample 1, ● Sample 2)
3. Silk Threads I
4. Cotton Threads I

The resistances are for a single 1.3 cm. length of thread or for a single twisted pair.

alternately expanded and constricted portions at regular intervals along their length. Where these variations in cross-section are large, the resistance of such a filament is determined by the parts of the filament whose cross-sectional area is least. The resistance of the whole filament is then practically independent of the amount of water in the expanded portions.¹ Thus wool could have a higher resistance than cotton for a given moisture content if the structure of wool is such that the moisture is distributed in filaments having constricted parts of smaller cross-section than similar constricted parts in the elementary conduction filaments in cotton. It would also be expected that

¹ Cf. Evershed's "dormant" and "resistance" water.—S. Evershed: loc. cit.

the narrower the constrictions in such filaments the more rapidly would the resistance of the filament vary with moisture content because the percentage change in cross-sectional area of the constricted parts, for a given increment of moisture, would be greatest for the filaments having the narrowest constrictions. That the behavior of these textiles is consistent with this explana-

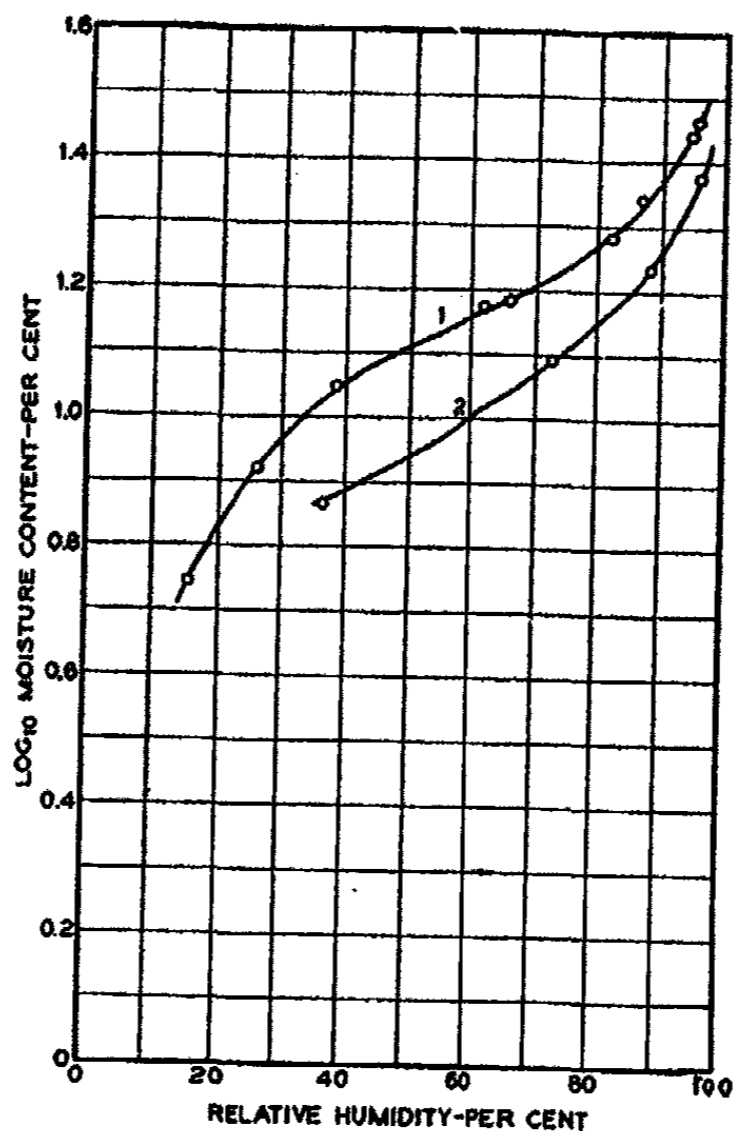


FIG. 13

The Moisture Content of Wool and Silk as a Function of Relative Humidity Interpolated to 25°C. from Schloesing's data.

1. Wool

2. Silk

tion is shown by the fact that the resistance varies with moisture content most rapidly for the textiles which combine relatively high hygroscopicity with relatively high resistance (Fig. 12). The relative insulating qualities of textiles, therefore, are determined not only by their hygroscopicities, but also by the resistance of the moisture as distributed within them, and by the rate of variation of resistance with moisture content.

Summary

Data are given showing the variation of the insulation resistance of cotton, silk and wool samples with relative humidity and moisture content. The samples consisted of short threads, individual fibers and standard cotton insulated wires. Some of these samples contained more electrolytic impurities

than others. The results therefore show the effect of differences in the form and electrolyte content of the samples on the resistance-humidity relationship. The insulation resistance of any cotton sample is about 10^{12} times greater at 1% relative humidity than at 99%, and in the range 20-80% is an exponential function of relative humidity. The rate of change of insulation resistance with relative humidity is independent of the form of the sample and of its electrolyte content. A decrease in the electrolyte content of the cotton causes an increase in the general level of resistance, i.e., a displacement of the resistance-humidity curve parallel to itself. The conductance of a cotton thread is equal to the sum of the conductances of the fibers of which it is composed and the resistance of a cotton thread is directly proportional to its length. These facts indicate that in spite of its fibrous structure cotton has a fairly definite resistivity. When the resistance measurements are made both in the order of increasing and of decreasing relative humidity the resistance-relative humidity curve is a closed loop whose sides are almost parallel in the range 20-80%. The logarithmic plot of the insulation resistance of cotton samples as a function of their moisture content gives a system of parallel straight lines, indicating that the resistivity of cotton is a power function of its moisture content. This shows also that in the resistance-humidity curve the loop and the inflections at 20 and 80% relative humidity are due to the relationship between moisture content and humidity rather than resistance and humidity. Equations are given by which the resistance of a cotton sample can be calculated for any moisture content (or the relative humidities corresponding to it) provided a measurement has been made at a single moisture content. The regular dependence of the resistivity of cotton on its moisture and electrolyte content and the relatively small variation of resistance from one sample to another of the same material suggest that the distribution of moisture corresponds to some regularity in the structure of the textile, e.g., in that of cellulose in the case of cotton. The insulation resistance of silk and wool samples is also a power function of their moisture contents. The resistivity of silk depends on its electrolyte content in the same way as that of cotton. The rate of change of resistivity with moisture content is much greater for silk and wool than for cotton. For a given moisture content the resistivity of silk or wool is greater than that of cotton though silk and wool are more hygroscopic than cotton. The investigation of cotton was not extended below about 1% relative humidity and that of silk and wool not below about 40% so it is not definitely known whether these relationships hold at humidities lower than these.

It is suggested that the conducting water-paths in a textile consist in effect of elementary filaments which have alternately expanded and constricted sections along their length, forming a regular space-pattern whose elements have different dimensions for different textiles. The resistivity of the textile is then determined by the cross-sectional area of the narrowest parts of the path rather than by the total moisture content; thus, by assuming that the constricted parts of the filaments are smaller in silk and wool than in cotton the higher resistivity of these materials for a given moisture

content is explained. The rapidity of the variation of resistivity with moisture content can also be explained in this way.

This work forms part of an investigation of the insulating properties of textiles which was initiated by Mr. R. R. Williams. We are particularly indebted to him for the suggestion of the study of the relation of the individual fibers to the textile as a whole and of the effect of humidity on insulation resistance.

We also wish to take this opportunity to thank Dr. H. H. Lowry for his very helpful interest in the work and for valuable assistance in the interpretation of the results and the preparation of this paper.

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1787-

THE ELECTROLYSIS OF SODIUM SULPHIDE SOLUTIONS

BY WALTER RAYMOND FETZER

The periodic phenomena occurring at the anode in a solution of sodium sulphide, studied in Küster's laboratory, have attracted wide attention; but no quantitative explanation of their occurrence has yet been advanced. None of the experimenters used solutions of known contents, worked in the absence of air, studied the influence of current density, knew what the products of electrolysis were, or investigated the possible effect of these products and of thiosulphate (formed in polysulphide solutions exposed to the air) on the phenomena. In the explanation put forward by Küster,¹ he assumed that increasing the polysulphide content of a sulphide solution lessened the current needed to precipitate sulphur; the experiments detailed below show that this assumption is erroneous. But the relations disclosed by these experiments were so unexpected, and are themselves so much in need of coordination and explanation, that it seems premature to attempt to build on them an explanation of the still more complicated phenomena studied by Küster. The whole subject of electrolysis of sulphide solutions evidently needs further study; the work here described was carried out in 1920-22, but the publication of this paper has been deferred in the hope of completing and extending it. As it now seems unlikely that I shall have an opportunity to do so, the results here presented are put forward as a first contribution.

My acknowledgments are due to Professor W. Lash Miller, under whose direction this investigation was carried out, to Mr. J. H. Ratcliff who helped me with some of the measurements, and to Professor J. T. Burt-Gerrans and Dr. A. R. Gordon.

Preparation of the Reagents

Carbonate-free sodium hydroxide solution: The chemical sold as "C. P. electrolytic sodium hydroxide" contains a considerable amount of carbonate (over 1%), the removal of which from strong solutions (4-Normal) by baryta or by lime is impractical, because part of the baryta stays in solution, while the lime forms a suspension difficult to filter. Küster's method of preparing carbonate-free solutions by the action of water on sodium and Jorissen's electrolytic apparatus² are not practical when large quantities are required.

My own solutions were made in a small laboratory rocking cell of the Castner-Kellner type. This cell is made of glass and is covered by a steel plate to the under side of which is cemented a sheet of rubber steam packing, which had been boiled out with sodium hydroxide solution and then coated with paraffin wax; it is divided into three compartments (each about 12 cm. wide \times 13 cm. long \times 11 cm. deep) by two partitions which reach within 3

¹ Küster: Z. anorg. Chem., 46, 113 (1905).

² Jorissen: Chem. Weekbl., 6, 145 (1909).

mm. of the bottom of the cell and are cemented¹ to its sides. A glass plate 6 mm. thick is cemented to the bottom of each compartment; it reaches from wall to wall, but ends about 2 mm. from the partitions. Six and a half kilos of mercury are sufficient to keep the aqueous solutions in the three compartments from mixing with each other when the cell is rocked. The two end compartments were provided with platinum anodes 6×6 cm., and were charged with approximately 4 N solution of sodium hydroxide (about 600 cc. each); the centre compartment held a nickel gauze cathode, 5×10 cm.; the air in it was freed from carbon dioxide and it was charged with freshly boiled distilled water (usually about 800 cc.). Current entered the cell through the two platinum anodes, in series with each of which was a small variable resistance in order to equalize their amperage. Part of it left via the gauze cathode in series with which was the main rheostat; and part through a glass-insulated platinum wire which dipped into the mercury in the centre compartment. Before allowing any current to flow through the gauze, it was necessary to saturate the mercury with sodium, otherwise oxide of mercury would be formed in the centre compartment; this required about 35 g. sodium, or a current of 10 amperes through the platinum wire for 4 hours. Ten amperes was then sent through the gauze and the wire-current was reduced to 2 amperes; sodium hydroxide corresponding to 100 cc. of 4 N solution was formed every hour, and an accurate determination showed an overall current efficiency of 97%.

Sodium Monosulphide solution: The commercial salt always contains traces of polysulphide and thiosulphate; my solutions were prepared by passing hydrogen sulphide into a measured volume (815.5 cc.) of carbonate-free sodium hydroxide solution until the increase in weight corresponded to the formula NaSH, and then adding an additional 815.5 cc. of the hydroxide solution. This operation was carried out in a three-necked bottle; the weight of the solution before and after adding the gas was determined on a balance which read to 0.01 g.; a second Woulff bottle served as counterpoise. The gas was passed in at a rate of about 7 g. per hour; it was purified by passing through a train of three small wash bottles containing sodium hydroxide and one containing glycerine, and two calcium chloride drying towers; oxygen was removed from the train before the Woulff bottle was attached by passing hydrogen sulphide through it for half an hour. The two exactly equal portions of sodium hydroxide solution were obtained by means of a large pipette, filled and discharged through a 3-way tap at the bottom; the stem of the pipette was attached to a soda lime tube. By filling the pipette for the second time immediately after the first portion had been withdrawn, temperature corrections were avoided; five minutes was allowed for drainage. Direct weighing showed that the amounts of 4 N NaOH solution delivered from two successive fillings agreed within 0.05%.

In spite of the precautions taken, the acid sulphide often had a slight yellow tinge; but the amount of thiosulphate and polysulphide formed was

¹ Shoemaker's wax serves well for repairs.

found by analysis to be negligible. The monosulphide solution was kept over mercury in an atmosphere of hydrogen to prevent the formation of polysulphide, and to remove any traces that might be formed.

Methods of Analysis

The solutions to be analysed were solutions of sodium monosulphide or acid sulphide and those resulting from their electrolysis; as tri- tetra- and penta-thionates and persulphates are decomposed by alkaline sulphides, their salts are excluded; sulphites also are excluded because they react instantaneously with polysulphides to form thiosulphate.¹ Thus the solutions may contain sodium monosulphide, polysulphide, thiosulphate, sulphate and dithionate together with either sodium hydroxide and carbonate or sodium acid sulphide. In applying the methods of analysis given below it must not be forgotten that solutions of the sulphides absorb oxygen from the air forming polysulphides, and that polysulphides are rapidly oxidized to thiosulphate by the air.

Thiosulphate, sulphate, and dithionate were determined after removing the sulphides by zinc nitrate and oxide; polysulphide by conversion into thiocyanate (a correction must be made for the thiosulphate.) In solutions free from polysulphides, the sulphides, hydroxide and carbonate were determined by iodine; but if polysulphide were present, the total sodium was determined by conversion to the hydroxide by means of cuprous oxide. The quantities of reagents given below are suitable for solutions about four times normal with respect to Na_2S or NaSH (i.e. containing about 156 g. of Na_2S per liter).

Automatic pipette: For each analysis 5 cc. of the solution was transferred from the cell to the centrifuge tube, or to a beaker, by means of a water-jacketed pipette provided with a 3-way tap at the lower end and a two-way tap (which could connect the interior with a vacuum pump or with a nitrogen supply) at the upper end. The pipette was filled by means of the vacuum, nitrogen was then admitted and the contents allowed to flow out; two minutes were allowed for draining and the outflow tube was rinsed with water. The pipette was calibrated by titrating the amount of 4 N sodium hydroxide it delivered and determining the specific gravity of the solution; successive portions agreed within one-tenth of one percent.

Removal of Sulphides: About 1 g. of zinc oxide and 1 g. of zinc carbonate were added to 30 cc. of approximately normal zinc nitrate solution, shaken to form a milky suspension, and poured into a cylindrical glass centrifuge tube of about 130 cc. capacity. The tube was filled with water to the mark (about 85 or 90 cc. total volume), stirred again and centrifuged; after which the clear liquid was decanted through a folded filter. The residue in the centrifuge tube was washed six times by adding water to the mark, centrifuging and decanting through the filter paper; the total volume of the filtrate was about 600 cc. The zinc oxide is added to neutralize the nitric acid formed when

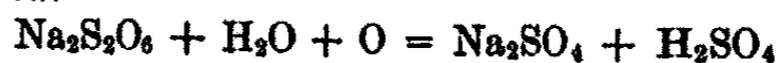
¹ A method for determination of sulphites based on this reaction has been proposed by Billeter: *Chem. Ztg.*, 39, 500 (1915).

acid sulphide is present; but even when there is no acid sulphide, the addition of a little oxide is advantageous, as without it the precipitate is apt to stay suspended in the wash water. Addition of zinc carbonate lessens the adsorption of sulphate by the precipitate; without this addition as many as twenty washings may be required to get all of the sulphate into solution.

Determination of Thiosulphate: This was effected volumetrically by means of fifth normal iodine solution, after the sulphides had been removed.

Determination of Sulphate: The solution after sulphide had been removed was heated to boiling, and a five per cent solution of barium chloride was added in slight excess. The mixture was let stand at 50°-60° overnight, filtered, and the filtrate reserved; the precipitate was washed thoroughly with dilute hydrochloric acid and distilled water, dried and weighed.

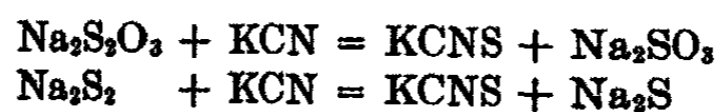
Determination of Dithionate: Thiosulphate is removed, as mercuric sulphide, by mercurous chloride. Dithionate is converted into sulphate and sulphite by heating with hydrochloric acid, but in the presence of nitrates (introduced as zinc nitrate during the removal of the sulphides) nothing but sulphate is formed:



To the filtrate from the sulphate determination was added 2 g. to 10 g. of mercurous chloride (depending on the amount of thiosulphate present) and 2 g. of barium carbonate; the whole was boiled for five minutes, allowed to stand for several hours, and decanted through a filter. The residue was washed three times by decantation, and then the precipitate was washed on the filter three times with distilled water. To the filtrate was added 15 cc. concentrated hydrochloric acid, and the solution was evaporated almost to dryness on a water bath; baking was avoided. The residue was taken up in water, made up to 400 cc., and the sulphate determined as barium sulphate.

The results are satisfactory; but a blank is desirable in case the hydrochloric acid used should contain traces of sulphuric. Exactly half a gram of recrystallized sodium dithionate ($\text{Na}_2\text{S}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$) on evaporating with hydrochloric and nitric acids gave barium sulphate corresponding to 0.5031 g.; 0.5031 g.; when the procedure given above was followed, the barium sulphate corresponded to 0.5023 g.; and when 25 cc. fifth-normal sodium thiosulphate was added before the mercurous chloride, to 0.5024 g.

Determination of Polysulphide: On warming with potassium cyanide, solutions of thiosulphate¹ or polysulphide² react to form sulphocyanates; dithionates³ do not react; and Gutmann has shown that sulphites do not interfere.



Five cc. of the solution is added to 1 cc. of a saturated solution of potassium cyanide in the 120 cc. centrifuge tube (see "Separation of Sulphides") and

¹ Gutmann: Z. anal. Chem., 46, 485 (1907).

² Joannis: Ann. Chim. Phys., (5) 26, 534 (1882); Feld: J. Gasbel., (1903) 604; Z. anal. Chem., 42, 708 (1903).

³ Gutmann: Ber., 39, 509 (1906).

digested for ten minutes in a steam bath. To the colourless liquid is added about 35 cc. of cold water and 30 cc. of normal zinc nitrate solution, the mixture is stirred and centrifuged, and the supernatant liquid decanted through a folded filter. Half a gram of zinc oxide is added to the residue in the centrifuge tube, and water to the mark; the whole is stirred, centrifuged and decanted as before; this washing is repeated five times more. To the filtrate (about 600 cc.) is added 5 cc. of a ten percent nitric acid solution and six drops of ferric nitrate indicator. The sulphocyanate is determined in the usual manner with decinormal silver nitrate. As the thiosulphate has already been determined (see above) the polysulphide can be obtained by difference.

Commercial potassium cyanide contains iron; and its solution on standing deposits ferric hydroxide, which later on may give rise to a blue coloration. If iron-free cyanide is not available, a fresh solution should be made for up each set of determinations. The reaction between cyanide and polysulphide is almost instantaneous; that with thiosulphate is slower, and if much thiosulphate be present the digestion should be prolonged. Zinc nitrate precipitates not only the sulphide but also the excess of cyanide and an odour of hydrocyanic acid is generally noticeable after filtration; this does not affect the accuracy of the determination, but may make the end-point harder to obtain. Zinc oxide is added to flocculate the precipitate, and prevent it remaining suspended in the solution; with this addition, 3 to 5 minutes centrifuging at a speed of 800-1000 r.p.m. is sufficient. The ferric nitrate indicator was prepared by boiling iron nails in nitric acid until no more brown fumes were evolved; the syrupy solution solidified on cooling, and enough water was added to form an almost saturated solution.

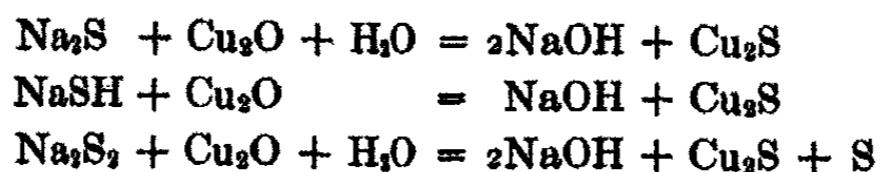
The accuracy of the method was checked by dissolving weighed amounts of sulphur in 4 N sodium sulphide; taken: 0.2938 g., 0.1088 g.; found: 0.2935 g., 0.1083 g.

Determination of Monosulphide with either Acid Sulphide or Hydroxide and Carbonate (in the absence of Polysulphide): This is the usual method based on the amount of iodine required to oxidize the sulphur and on the acidity of the resulting solution.



To 125.00 cc. fifth-normal iodine and 100.00 cc. fifth-normal hydrochloric acid, water is added to make the volume 400 cc.; and then with constant stirring, 5 cc. of the solution to be analysed. Excess iodine is determined by fifth-normal thiosulphate; phenol-phthalein is added and fifth-normal sodium hydroxide to colour; then methyl-red and fifth-normal acid until the methyl-red endpoint is reached (this gives the carbonate if any). From the iodine used up, must be subtracted the amount required by the thiosulphate (already determined; see above).

Determination of total Sodium as Sulphide, Polysulphide, Hydroxide, and Carbonate: Solutions of monosulphide and polysulphide react with cuprous oxide precipitating cuprous sulphide and leaving the sodium in the solution as the hydroxide.



About 6 g. of cuprous oxide are suspended in 100 cc. of water, 5 cc. of the solution is added and thoroughly stirred; the precipitate is allowed to settle and decanted through a filter; then washed three times in the beaker using 100 cc. water for each washing; and finally given a thorough washing on the filter paper. The filtrate is titrated with fifth normal acid, by the double beaker method, using methyl-red as indicator.

Cuprous oxide was chosen in preference to others, because the precipitate is granular and settles rapidly; the dry commercial salt was used; it must be free from cupric oxide, for Debus has shown that this oxidizes polysulphide to thiosulphate.

The results are very satisfactory; the amount of acid required for 5 cc. of 4 N sodium monosulphide solution is not changed by dissolving half a gram of sulphur in the sulphide solution before adding it to the cuprous oxide.

The Products of Electrolysis

Very little has been published as to the products of electrolysis of solutions of the alkali sulphides. (i) Durkee¹ shewed that prolonged electrolysis of a sodium sulphide solution or of a sodium hydrogen sulphide solution converts it quantitatively into sulphate; and gives a table and graph of the content of sulphate, sulphide, thiosulphate and alkali in the electrolyte (originally sodium sulphide) as a function of the amount of electricity that had been passed through the cell. Not much can be made of his results; in the first place, the method of analysis employed does not distinguish between monosulphide and polysulphide, or between thiosulphate and dithionate; in the second place, the electrodes consisted of two cylinders of platinum foil standing in a beaker, so that although the current was kept constant, the current density was different at different parts of the electrode surface; and in the third place, no precaution was taken to exclude air although air rapidly converts polysulphide to thiosulphate, and the original solution of sodium sulphide was not examined for the presence of thiosulphate. (ii) Scheurer-Kestner² attacked Durkee's conclusion that thiosulphate was one of the products of electrolysis of sodium sulphide solution, and asserts that "the reaction is simply $\text{Na}_2\text{S} + \text{O}_4 = \text{Na}_2\text{SO}_4$." The paper contains no new experimental results, but quotes from a previous³ publication; on examining this it appears that except in one experiment the current was not measured, that no precautions were taken to exclude air, and that the absence of thiosulphate was established, not by analysis but by a very insecure deduction based on measurements of the time required to completely oxidize solutions

¹ Durkee: Am. Chem. J., 18, 525 (1896).

² Scheurer-Kestner: Bull., (3) 17, 99 (1897).

³ Schuerer-Kestner: Bull., (2) 46, (1881).

of sulphide and thiosulphate respectively. (iii) Brochet and Ranson¹ electrolysed solutions of potassium and sodium sulphide containing thiosulphate as impurity; under the conditions of their experiments the main product of the electrolysis was polysulphide, no sulphate was formed, and the amount of thiosulphate in the solution was unaffected by the electrolysis. No attempt was made to relate the amount of polysulphide formed to the amount of electricity that passed through the solution, but from a statement that appears at the foot of the table on page 510 it appears that 0.544×96500 coulombs decomposed 8.5 g. of crystallized sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), that is, one faraday decomposed 0.065 Na_2S . Under certain conditions sulphur was precipitated at the anode, and these authors were the first to observe (though not the first to publish) the periodic phenomena studied by Küster² and his pupils (see below, p. 0000). (iv) Küster himself noted the formation of polysulphide, but did not record his currents, and made no attempt to analyse the electrolyte.

From these results it appeared probable that the primary product of electrolysis of sodium sulphide solution would be polysulphide, and the ultimate product of prolonged electrolysis, sulphate; whether thiosulphate is formed or not is disputed, and no attempt has been made to detect the presence of dithionate, although this substance is among the products of electrolysis of solutions of sulphite.³ Moreover no determination has been made of the "electrochemical equivalent of sulphur" in solutions of sulphides and polysulphides.

My own experiments may be divided into two groups, viz.—preliminary and quantitative.

Preliminary Experiments: In these, a solution of sodium monosulphide 4.3 N (i.e. containing 168 g. of Na_2S per liter) was electrolysed between platinum electrodes placed opposite one another in an open beaker.

(a) *Anode 3.7 × 2.2 cm.* With very low currents the solution touching the anode turned yellow and fell to the bottom of the beaker; no (solid) sulphur was deposited. When the current was increased to 0.13 amp. an irregular deposit of sulphur appeared on the anode and a voltmeter across the electrodes showed a sudden rise of about 1.2 volts. On repeating this electrolysis with the same solution (which was now appreciably yellow in colour) the current could be increased to 0.57 amp. before sulphur appeared; further increase of the current up to 2.2 amp. did not cover the whole surface of the anode with sulphur.

(b) *Anode 0.7 × 0.5 cm.* In a fresh solution of the same concentration, 0.08 amp. covered the whole surface with sulphur; the current was increased in steps of about 0.05 amp., and when 0.6 amp. was reached the surface was still covered, but the yellow solution began to stream upwards instead of downwards as previously; with 0.8 amp. pieces of sulphur broke loose from

¹ Brochet and Ranson: *Z. Elektrochemie*, 9, 509 (1903).

² Küster: *Z. anorg. Chem.*, 46, 113 (1905).

³ Förster and Friessner: *Ber.*, 35, 2515 (1902); Friessner: *Z. Elektrochemie*, 10, 265 (1904).

the anode and were carried upward by the convection current, but even when the current had been raised to 3.6 amp. some sulphur still adhered to the middle of the anode.

(c) *Anode, a wire 0.8 cm. long by 0.1 cm. in diameter (0.25 cm.² surface).* In a fresh solution of the same composition as before, 0.07 amp. covered the whole surface with sulphur; with 0.35 amp. the sulphur began to break loose; with 0.7 amp. there was very noticeable upward convection; with 1.0 amp. the surface was free from sulphur except at the lower tip and where the wire was sealed through its glass tube holder; with 1.4 amp. all the sulphur had disappeared. With still higher currents, bubbles of gas (presumably oxygen) could be seen rising with the convection current; but the lower limit at which this gas appeared could not be fixed with accuracy.

Thus there seem to be three stages in the electrolysis, which follow one another as the current density is increased, but the current density at which the change from one to another occurs evidently depends on the amount of polysulphide in the electrolyte and on the form of the anode; the effect of the latter is probably due to its influence on convection. These are: *First stage*:— formation of polysulphide and no deposit of sulphur. *Second stage*:— formation of polysulphide and deposition of sulphur. *Third stage*:— formation of polysulphide and no deposition of sulphur; at the close of the second stage, the sulphur deposited on the anode breaks loose and is carried away by the convection current, and during the third stage oxygen may be liberated.

The following experiments show that during the first and second stages, nothing but sulphur and polysulphide are formed; in the third stage, polysulphide, sulphate and dithionate; no thiosulphate was found in any of the quantitative electrolyses.

Quantitative Experiments: In these experiments two different electrolytic cells were used.

(a) *Electrolytic cell with diaphragm and rotating anode:* The anode consisted of a brass cylinder 51 mm. high and 20 mm. in diameter which was electroplated first with copper and then with platinum and burnished. It was mounted on a vertical shaft, the rest of whose surface was covered by glass tubing; the joints between the metal and the glass were protected by hard rubber caps cemented to the shaft by shoemaker's wax. The cathode compartment held 53 cc. and consisted of the annular space between a copper cylinder (on the outside) and a porous porcelain cylinder 52 mm. high \times 33 mm. internal diameter, which acted as diaphragm; the inner surface of the copper, 52 mm. high \times 60 mm. diameter, was platinum-plated and formed the cathode, the outer surface was wrapped with electrician's tape and coated with paraffine wax. Top and bottom of the cathode compartment were covered by hard rubber discs, that at the bottom being provided with three legs 17 mm. long; and the whole stood, on these three legs, on the bottom of a cylindrical glass jar 155 mm. high and 85 mm. in diameter. The anode rotated in the axis of the porcelain cylinder, so that the anode compartment completely surrounded the cathode compartment and consisted of all the

space within the glass jar except that bounded by the copper and porcelain cylinders and their rubber discs; when 500 cc. anolyte were contained in the cell the cathode compartment was completely covered, and the solution reached 35 mm. above the top of its upper disc.

An iron ring cemented to the outside of the glass jar at the top was bolted through a rubber gasket to an iron disc, suitably perforated and insulated by a coating of paraffin wax, which served as a cover for the anode compartment. The anode shaft passed through a central opening in this cover, entry of air being prevented by a mercury seal. Two glass tubes passed, air-tight, through holes bored in the cover and in the upper disc of the cathode compartment, so that the latter could be filled and emptied; one of these tubes served also for the escape of the hydrogen generated during electrolysis. Electric connection to the cathode was made through a third tube. There were three more holes through the cover, one admitted a tube to fill the anode compartment, and one led to the automatic pipette (see p. 1789); the third enabled the level of the anolyte to be determined exactly (by means of a wire making contact with the surface of the liquid, and a voltmeter) so that if necessary correction could be made for any change in volume due to electrical endosmose, but in the event, such corrections proved unnecessary.

An atmosphere of nitrogen (freed from oxygen by pyrogallol) was maintained in the cell, the gas entering through a branch of the tube used to fill the anode compartment. The anode was rotated by an electric motor, whose speed of rotation was determined by revolution counter and stop watch; and the whole apparatus was mounted on a frame attached to the wall of the laboratory in such a manner that the cell could be lowered into the water of a thermostat.

(b) *W-shaped cell*: This was formed of a piece of glass tubing 70 cm. long and 2 cm. in diameter; outlets were provided at the bottom of the two side arms and one at the top of the inner loop of the *W*; it held 150-160 cc. conveniently. To reduce convection, plugs of glass wool were inserted in the anode side-arm, and in some cases the top of the inner loop was filled with a more dilute solution of the electrolyte. Platinum electrodes were mounted through corks which closed the upper ends of the two outside arms; and for the experiments with sodium acid sulphide, the cork supporting the anode was perforated for a tube to carry the hydrogen sulphide to the absorption apparatus. This consisted of a wide beaker charged with a solution of cadmium sulphate and slowly rotated round its vertical axis; the hydrogen sulphide tube passed air-tight through the stem of an inverted funnel and reached almost to the opening of the latter. When this absorption unit was to be employed, the opening of the funnel was brought just below the surface of the solution in the beaker and the air between the funnel walls and the solution was removed by suction; it was thus possible to bubble gas through a column of liquid 2-2.5 cm. high without creating pressure in the electrolytic cell, and any bubbles that passed through were trapped above the absorbing liquid instead of escaping to the atmosphere. The precipitated cadmium sulphide was filtered off, washed, dried and weighed.

Electrolysis of Sodium Sulphide solution with low current density: After a number of preliminary determinations to become familiar with the apparatus, a final electrolysis was carried out in cell (a) with all precautions: temperature 20°C.; initial solution Na₂S, 4.5 N (i.e. 2.25 Na₂S per liter); speed of rotation of the anode, close to 500 r.p.m.; current 1.85 amperes (corresponding to 130 scale divisions on a Weston instrument Model 45, provided with special shunts and calibrated against a laboratory standard instrument, by means of a Leeds and Northrup potentiometer). The cathode compartment was filled first; and after an interval to saturate the porcelain, 500 cc. of the electrolyte was measured accurately into the anode vessel. The polysulphide liberated was determined in duplicate after exactly six, nine and twelve hours; and at the close of the run the anolyte was found to be free from thiosulphate, sulphate, and dithionate. The amounts of polysulphide sulphur formed corresponded to the electrochemical equivalent S/2, i.e. 16.03 g. of sulphur per faraday; they were:

| | | |
|---------|-----------------------|------------------------|
| 6 hours | obs. 0.412 × 16.03 g. | calc. 0.414 × 16.03 g. |
| 9 " | " 0.619 | " 0.621 |
| 12 " | " 0.815 | " 0.828 |

The "limiting current" experiments detailed below show that during most of this electrolysis sulphur must have been precipitated on the anode (it was all redissolved in the anolyte, however, and so did not escape the analysis) and the conclusion to be drawn is, that during the first and second stages of electrolysis of sodium sulphide solution, and of solutions containing some polysulphide, polysulphide is formed at the rate of S/2 per faraday, and that there is no other product of electrolysis.

Electrolysis of Sodium Disulphide solution with low current density: Cell (a) was used; the anolyte was made by dissolving in approximately 4.5 N sodium sulphide solution the quantity of washed and dried sulphur calculated to bring the ratio of sodium to sulphur in the solution close to that given by Na₂S₂; the cathode compartment was filled with 4.5 N sodium sulphide. Experimental procedure was the same as in the previous electrolyses; temp. 20°C., rate of rotation 500 r.p.m., current 1.77 amp., volume of anolyte 500 cc., volume of catholyte 60 cc. At the close of the electrolysis the anolyte was examined for thiosulphate, sulphate and dithionate, and none were found. The amounts of polysulphide sulphur formed during the electrolysis were:

| | | |
|---------------|-----------------------|------------------------|
| After 6 hours | obs. 0.436 × 16.03 g. | calc. 0.396 × 16.03 g. |
| " 9 " | " 0.604 | " 0.594 |
| " 12 " | " 0.776 | " 0.792 |

the "calculated" values being obtained on the assumption that 16.03 g. sulphur (as polysulphide) is formed by the passage of one faraday through the solution. According to the "limiting current" determination given below, no sulphur was precipitated during the electrolysis; the ratio of sodium to sulphur in the anolyte at the close of the experiment was close to that represented by the formula Na₂S₃.

Trouble was caused by the crystallization of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in the cathode compartment; moreover, the amount of polysulphide sulphur had to be found by subtracting two large numbers, viz. polysulphide in the solution after, and before, electrolysis; so, although the observed results differ appreciably from those calculated, it seems safe to infer that the only result of the electrolysis was the formation of one equivalent of polysulphide ($\text{S}/2$) per faraday.

Stage 3 of the electrolysis of Sodium Sulphide solution: Some fifteen electrolyses (all with approx. 4.5 N Na_2S solution) were carried out with high current densities in cell (b); it was found difficult to avoid variations in the current, and therefore a copper coulometer was introduced in series with the cell. The anode consisted of a piece of No. 22 platinum wire $3/8$ inch long (0.19 cm.² in area). Two glass-wool plugs in the anode compartment helped to reduce convection; at the close of the electrolysis the outlet at the top of the inner loop of the *W* was opened to admit air, and the anolyte was drawn off for analysis; in a few cases when the yellow coloration extended into the cathode side, most of the colourless cathode solution was pipetted off, and the polysulphide in the remainder was determined.

The preliminary experiments make it clear that in the *W* cell a vigorous convection current is set up at the anode, and it is obvious that the composition of the solution actually touching the anode must depend on the direction and intensity of this current; as in the *W* cell there was no artificial stirring, the degree of convection must depend upon "accidental" circumstances, such as the perpendicularity of the anode wire, its distance below the surface of the electrolyte, etc.; it is, therefore, hardly surprising that even when the electrolyte the current density and the duration were the same in two experiments, the amounts of polysulphide sulphate and dithionate formed should be found to vary. To make a thorough study of this stage of the electrolysis it would clearly be necessary to employ artificial stirring; the use of cell (a) was excluded, as the surface of its rotating anode was so large that well over a hundred amperes would be needed to bring the electrolysis to the third stage; the results given in Table I must therefore be regarded as merely a first step towards the solution of this problem. They serve to show that when the current density was below 8 amp. per sq. cm. of anode surface, the sum¹ of the amounts of polysulphide, sulphate and dithionate formed during the electrolysis is equivalent to the amount of copper deposited in the coulometer; with higher current densities, the sum is less, no doubt owing to the evolution of oxygen. Comparison of numbers 3 and 5 with number 4 (Table I) shows that the amount of polysulphide may vary when the electrical conditions remain the same.

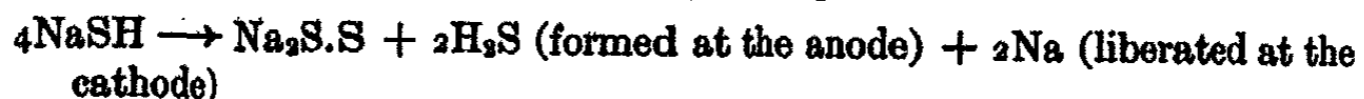
Electrolysis of Sodium Acid Sulphide solution (NaSH): With very low current density (rectangular platinum anode, 0.035 amp. per cm.²) no sulphur

¹ The amounts of copper, polysulphide, sulphate and dithionate formed are expressed in faradays: 63.6 g. copper = $\text{Cu} = 2$ faradays; 32 g. sulphur = $\text{S} = 2$ faradays; $\text{SO}_4 = 8$ faradays; $\text{S}_2\text{O}_6 = 14$ faradays. Thus, in Table I No. 1, the weight of copper deposited in the voltameter was $0.0798 \times 63.6/2$ g.; that of polysulphide sulphur was $0.0508 \times 32.06/2$ g. and that of sulphate ion was $0.0280 \times 96.06/8$ g.

TABLE I

| No. | Average Current | Cu | S | SO ₄ | S ₂ O ₄ | S ₂ O ₃ | Total |
|-----|-----------------|--------|--------|-----------------|-------------------------------|-------------------------------|--------|
| 1 | 0.92 amp. | 0.0798 | 0.0508 | 0.0280 | | 0 | 0.0788 |
| 2 | 1.61 | .0898 | .0637 | .0245 | 0.0037 | 0 | .0886 |
| 3 | 1.93 | .1439 | .0525 | .0596 | .0088 | . | .1209 |
| 4 | 1.96 | .1255 | .0825 | .0225 | .0015 | 0 | .1065 |
| 5 | 2.01 | .1502 | .0561 | .0643 | .0061 | 0 | .1265 |
| 6 | 2.13 | .1585 | .0550 | .0605 | .0128 | 0 | .1283 |
| 7 | 2.49 | .0928 | .0586 | .0128 | .0010 | . | .0714 |

was deposited and the anolyte turned yellow; with higher current densities sulphur was deposited, and with still higher disappeared, as in the case of monosulphide solutions; in these cases the solution after electrolysis contained sulphate as well as polysulphide. Hydrogen sulphide was given off at the anode; quantitative determinations (third stage of the electrolysis) made with the absorption apparatus described under cell (b), shewed that for every gram of polysulphide sulphur formed, two grams of sulphur appeared as hydrogen sulphide. This relation is expressed by the equation—



The only reference to the electrolysis of sodium acid sulphide I can find in the literature is incidental to a study of thiopropionic acid by Bunge¹; he found that sulphur and hydrogen sulphide were formed at the anode. Bloxam² states that sulphur dissolves in solutions of sodium acid sulphide forming polysulphide and liberating hydrogen sulphide.

The "Limiting Current", that is, the Current needed to liberate Sulphur

All of these experiments were carried out under an atmosphere of nitrogen in cell (a), in which the platinum-plated anode had been replaced by a platinum cylinder 50 mm. high and 20 mm. in diameter mounted on the original shaft. Except when otherwise stated, the temperature was $20.0 \pm 0.2^\circ\text{C}$.

The method of operation was as follows: The cell was filled, the temperature adjusted, and the rate of rotation of the anode was noted; a switch was closed, which sent a current through an ammeter in series with the cell; as soon as the ammeter could be read the switch was opened, meanwhile the voltage over the cell was read by an assistant. The cell was then left without current until the voltmeter came to zero (in case the of the sulphide solutions this took from 15 seconds to 2 minutes, depending upon the current that had been passed) after which the operation was repeated using a higher current. The results were graphed, volts against amperes; a sudden increase in the slope of the curve indicated the "Limiting Current", but in many cases this was so clearly indicated by the numbers themselves that graphing was unnecessary.

¹ Bunge: Ber., 3, 911 (1870).

² Bloxam: J. Chem. Soc., 77, 760 (1900).

Copper Sulphate solution: Before experimenting with the sulphide solutions, the cell was filled with a solution of copper sulphate in maximum-conducting sulphuric acid, which contained 1.718 grams of copper per liter, and the "Limiting Current" for this solution (that is, the current that just brings the copper concentration at the cathode to zero) was determined as above for various rates of rotation of the electrode shaft. (In these experiments, of course, the rotating electrode was made the cathode). The results are given in Table II—limiting current in milamperes, rate of rotation in revolutions

TABLE II
(Copper Sulphate)

| | | | | | | | | | | | |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| r.p.m. | 192 | 290 | 301 | 400 | 490 | 504 | 510 | 575 | 662 | 812 | 817 |
| Lim. Ct. | 131 | 147 | 153 | 183 | 196 | 220 | 199 | 235 | 252 | 313 | 294 |
| $10^6 l$ | 525 | 468 | 449 | 376 | 351 | 312 | 345 | 292 | 273 | 220 | 234 |
| $10^6 l$ (calc) | 662 | 489 | 475 | 385 | 331 | 324 | 321 | 294 | 265 | 228 | 227 |

per minute. The thickness of the diffusion film in centimeters, l , was computed from LC (the Limiting Current in amperes), the copper concentration (1.718/31800 equivalents per cc.), the area of the rotating electrode (31.4 cm.²) and the diffusion constant¹ of copper sulphate in maximum-conducting sulphuric acid ($k = 4.2 \times 10^{-6}$ at 20°C.), by means of Eq. (1)²; all except

$$l = \frac{96500k \times \text{area} \times \text{conc.}}{LC} = 6.87 \times 10^{-4}/LC \quad (1)$$

the first (192 r.p.m.) agree within a few percent with those calculated from Eq. (2) which is of the usual form.

$$l \text{ (calc)} = 0.324(r.p.m.)^{0.74} \quad (2)$$

Sodium Monosulphide Solutions: The results of similar experiments with a 4.66 N solution of sodium monosulphide ($4.66 \times 39.08 = 182$ g. Na₂S per liter) are given in Table III. In this case there are not sufficient data to

TABLE III
(Sodium Monosulphide, 4.66 N)

| | | | | | |
|--------------------|-----|-----|-----|-----|-----|
| r.p.m. | 245 | 407 | 500 | 658 | 760 |
| LC obs. (milamp.) | 213 | 286 | 334 | 404 | 445 |
| LC calc. (milamp.) | 197 | 287 | 334 | 409 | 455 |

compute l ; but the agreement between the observed value of the limiting current and that calculated from the equation

$$LC \text{ (calc)} = 0.00336 \times (r.p.m.)^{0.74} \quad (3)$$

shows that the effect of the speed of rotation on the Limiting Current is exactly the same as in the case of the copper solutions. When the solution

¹ Burt-Gerrans (J. Phys. Chem., 30, 396 (1926)) found $k = 4.00 \times 10^{-6}$ at 18°C., A. R. Gordon (unpublished) found $10^6 k = 3.15$ at 7°C., 3.55 at 12°C., and 5.10 at 30°C.

² Rosebrugh and Lash Miller: J. Phys. Chem., 14, 830 (1910); see also Burt-Gerrans: *loc. cit.*

was diluted to something over double its volume (2.20 normal) the limiting current was less easy to determine, as the voltmeter readings were less steady. The results which are given in Table IV are therefore less accurate than those

TABLE IV
(Sodium Monosulphide, 2.20 N)

| | | | |
|---------------------------|-----|-----|-----|
| <i>r.p.m.</i> | 350 | 590 | 750 |
| <i>LC obs.</i> (milamp.) | 135 | 165 | 202 |
| <i>LC calc.</i> (milamp.) | 121 | 178 | 213 |

of Table III; the figures after "*LC(calc)*" were computed on the assumption that the limiting current is proportional to the 0.74 power of (*r.p.m.*) and (for a given speed of rotation) to the concentration of the sodium sulphide in the solution (see Eq. 4).

$$LC(calc) = 0.00336 (r.p.m.)^{0.74} \times 2.20/4.66 \quad (4)$$

The agreement between calculated and observed values justifies these assumptions.

These relations, if they stood alone, could be explained on the assumption that the polysulphide formed at the anode (and the experiments cited earlier in this paper prove that this is the only product) brought the concentration there to the composition $Na_2S_{2.4}$, which is that of the solution saturated with respect to sulphur (or more probably to Na_2S_3 , see p. 0000); employing the value for *l* found for the copper sulphate solution in the same apparatus, viz., that given by Eq. (2), this assumption leads (via Eq. 1) to the value $k = 2.3 \times 10^{-11}$ (or $k = 2.0 \times 10^{-11}$) for the diffusion constant of polysulphide sulphur,¹ which is that of a semi-colloid. Even if account be taken of the fact that polysulphide is an anion in such a solution, and therefore that diffusion is counteracted by migration, this value of *k* would not be materially increased.

Sodium Polysulphide solutions: The hypothesis just discussed, if extended without modification to include solutions containing polysulphide, makes two predictions, viz.:—(i) that (other things being equal) the more polysulphide the electrolyte contains, the lower the Limiting Current will be; and (ii) that the Limiting Current will increase with the rate of stirring and will be proportional to the 0.74 power of the number of revolutions of the anode per minute, exactly as in the case of the copper sulphate solution and the solution of sodium monosulphide.

The experimental results show that both of these predictions are wholly incorrect; (i) successive increases in the polysulphide content of the electrolyte first increase and then decrease the Limiting Current, and the maximum value of the latter (which is ten times that for pure monosulphide) is reached when the ratio of sulphur to sodium in the electrolyte is somewhat lower than that represented by the formula Na_2S_3 (see Table V and Fig. 1); and (ii) in

¹ This seems not to have been measured; a rough experiment showed that the diffusion is extremely slow.

TABLE V
(Sodium Polysulphide)

| | | | | | | | | |
|---------------------------------------------|------|------|------|------|------|------|------|------|
| Normality ¹ | 4.66 | 4.44 | 4.33 | 3.44 | 4.27 | 4.15 | 4.76 | 4.43 |
| x in Na_2S_x ² | 0 | 0.80 | 1.01 | 1.51 | 1.68 | 1.82 | 2.08 | 2.24 |
| LC (amp.) | 0.42 | 3.16 | 3.17 | 2.86 | 3.80 | 3.74 | 3.63 | 3.37 |
| LC corr. ³ | 0.38 | 3.04 | 3.12 | 3.56 | 3.80 | 3.85 | 3.27 | 3.25 |
| Normality ¹ | 3.84 | 4.27 | 4.28 | 1.95 | 1.96 | 1.96 | | |
| x in Na_2S_x ² | 2.72 | 2.79 | 2.95 | 1.00 | 1.25 | 2.38 | | |
| LC (amp.) | 2.13 | 1.92 | 1.58 | 1.33 | 1.55 | 1.56 | | |
| LC corr. ³ | 2.37 | 1.92 | 1.58 | 2.90 | 3.38 | 3.40 | | |

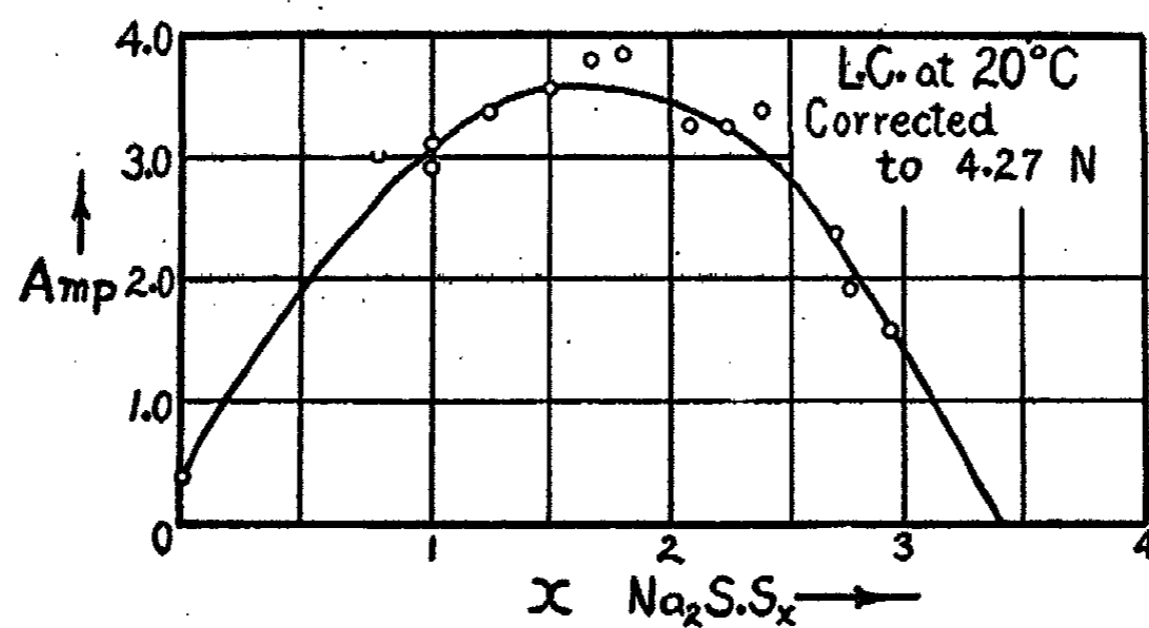


FIG. 1

the two cases that have been studied (viz.— $\text{Na}_2\text{S}_x\text{S}_{1.01}$ and $\text{Na}_2\text{S}_x\text{S}_{1.82}$) the Limiting Current is independent of large variations in the rate of rotation of the anode.

To extend the hypothetical explanation put forward for the results obtained with monosulphide solutions, so that it may account for the initial increase in LC produced by increasing the polysulphide content of the electrolyte, it might be assumed that the primary product of electrolysis, viz.: some semi-colloidal form of sulphur, reacts with some constituent of the polysulphide solution to form an easily diffusible compound; the greater the rate of this reaction, the greater the amount of sulphur that will be carried away by diffusion in a given time, and therefore the greater the Limiting Current. The further assumption that the rate of this reaction is proportional to the

¹ Normality = Equivalents of sodium per liter.

² Na_2S_x gives the ratio of sulphur to sodium in the solution taken for electrolysis.

³ The figures in this line were obtained from those after "LC(amp.)" by assuming that for a given polysulphide solution the Limiting Current was proportional to the normality. As shown below, this is fairly true for solutions in which the ratio of sulphur to sodium is not too high, while if the ratio approach Na_2S_2 , such an assumption is very unsafe. The "corrected" values are those for a normality of 4.27; this value was chosen because it is that of the two solutions with highest sulphur content. The "corrected" values of Table V are plotted in Fig. 1.

concentration of the primary sulphur, brings the case into a class discussed in Part III of the paper by Rosebrugh and Miller, and it is there shown (*loc. cit.* p. 867) that if the rate of this hypothetical reaction be great enough, a large change in the rate of rotation of the anode will have no effect on the stationary concentration of the primary sulphur, i.e. in the present case on the Limiting Current. The fact that the maximum Limiting Current was found when the electrolyte contained sulphur and sodium in the proportion given by $\text{Na}_2\text{S}_{2.7}$, suggests that sodium trisulphide might be taken as the "constituent" which reacts with the primary sulphur; if the rate of the reaction be proportional to some power of the concentration of this reagent as well as to that of the sulphur, the rate (and therefore the Limiting Current) should be greatest when in the reacting solution (*viz.*: that touching the anode) the concentration of trisulphide is at its maximum; this might well be the case when in the main body of the electrolyte the ratio of sodium to sulphur is less than that expressed by Na_2S_3 , because right at the anode, where sulphur is being generated, the ratio of sulphur to sodium must obviously be greater than it is in the external solution.

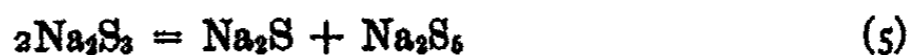
The effect of temperature on the Limiting Current was determined in the case of one solution only, *viz.*— $\text{Na}_2\text{S}\cdot\text{S}_{2.24}$, 4.13 N; the results are given in Table VI, a rise of 21.7 degrees increases the limiting current by 75%. This

TABLE VI
($\text{Na}_2\text{S}\cdot\text{S}_{2.24}$, 4.43 N)

| | | | |
|-----------|------|------|------|
| Temp. °C. | 9.3 | 19.9 | 31.0 |
| LC (amp.) | 2.42 | 3.37 | 4.22 |

is much less than the kinetic hypothesis just put forward would lead one to expect; on the other hand the fact that increasing the rate of rotation of the anode does not change the Limiting Current seems to exclude any other explanation; further measurements are obviously required.

Any attempt to carry this hypothesis into further detail must be based on assumptions as to the equilibrium existing between the trisulphide and the other constituents of a polysulphide solution. The simplest assumption, *viz.*: that the governing equilibrium is that represented by the equation



(the corresponding ionic equation might be written if preferred) requires that the trisulphide concentration, and therefore the Limiting Current, when graphed against x ($\text{Na}_2\text{S}\cdot\text{S}_x$ representing the ratio of sulphur to sodium *at the anode*) should be symmetrical about the ordinate at $x = 2$. Now the experiments show that the Limiting Current curve (Fig. 1) is fairly symmetrical about the ordinate $x = 1.7$ ($\text{Na}_2\text{S}\cdot\text{S}_x$ representing the ratio of sulphur to sodium *in the main body* of the electrolyte), and no simple assumption as to the mechanism of diffusion can convert one curve into another.

There is moreover a more serious objection to the assumption proposed, for according to it the value of x should be unaffected by diluting the elec-

trolyte, since according to Eq. (5) increase in volume should reduce the concentrations of all three constituents by the same fraction; this means that if any polysulphide solution be diluted with water to double its volume, the Limiting Current should be halved. Experiments show however that the effect of dilution is less simple than this, and that it depends upon the ratio of sulphur to sodium in the solution diluted. When $x = 0$ (monosulphide solution, Tables III and IV), when $x = 0.8$ (Table VII), when $x = 1.84$ (Table VIII) and when $x = 2.08$ (Table IX), the Limiting Current was found to be not far from proportional to the concentration of the solution; but when $x = 2.72$ and $x = 2.92$, dilution to double volume caused a rapid fall in the Limiting Current to half its original value, followed by a slower change to values lower still.

TABLE VII

 $(\text{Na}_2\text{S}.\text{S}_{0.8})$

| | | | |
|-------------------|------|------|------|
| Normality (N) | 4.44 | 3.05 | 2.24 |
| LC (amp.) | 3.16 | 2.12 | 1.63 |
| LC/ N | 0.71 | 0.70 | 0.73 |

TABLE VIII

 $(\text{Na}_2\text{S}.\text{S}_{1.84})$

| | | | | | |
|-------------------|------|------|------|------|------|
| Normality (N) | 4.23 | 3.72 | 2.97 | 2.08 | 1.04 |
| LC (amp.) | 3.61 | 3.13 | 2.52 | 1.72 | 0.91 |
| LC/ N | 0.85 | 0.84 | 0.85 | 0.85 | 0.88 |

TABLE IX

 $(\text{Na}_2\text{S}.\text{S}_{2.08})$

| | | | | | |
|-------------------|------|------|------|------|------|
| Normality (N) | 4.76 | 3.81 | 3.05 | 2.13 | 1.27 |
| LC (amp.) | 3.63 | 3.08 | 2.52 | 2.03 | 1.06 |
| LC/ N | 0.76 | 0.81 | 0.83 | 0.95 | 0.84 |

As there is no record in the literature of changes occurring in the properties of polysulphide solutions when kept at constant temperature in the absence of air, these measurements will be dealt with in the next Section.

Change with Time in the LC of a Sodium Polysulphide Solution

(i) *After diluting:* Powdered sulphur was shaken with a solution of sodium monosulphide (approximately 4 N) for 18 hours at room temperature; the composition of the solution so obtained was $\text{Na}_2\text{S}.\text{S}_{2.72}$, 3.84 N ; its LC was 1.12 amp. After the LC had been determined, one half the contents of the anode compartment was withdrawn and replaced by an equal volume of water; to ensure thorough mixing, the electrolyte was stirred vigorously with nitrogen and the anode was revolved at high speed; Table X gives the results of LC determinations made t minutes after the water had been added. Five minutes after diluting, the Limiting Current was 1.04 amperes, as compared with 2.12 amp. for the undiluted solution; but in an hour it had fallen to

0.55 amp. at which it remained. As a check, the portion of the original solution withdrawn from the cell was diluted with an equal volume of water and put away in a stoppered flask; 18 hours later its *LC* was found to be 0.54 amp. and after 3 hours more, 0.53.

TABLE X
($\text{Na}_2\text{S}\cdot\text{S}_{2.72}$, 1.94 N)

| | | | | | | | | | | | | |
|--------------------|------|------|------|------|------|------|------|------|------|------|------|------|
| <i>t</i> (minutes) | 5 | 14 | 30 | 43 | 60 | 85 | 130 | 175 | 902 | 914 | 940 | 1113 |
| <i>LC</i> (amp.) | 1.04 | 0.70 | 0.60 | 0.57 | 0.55 | 0.55 | 0.55 | 0.55 | 0.61 | 0.57 | 0.57 | 0.55 |

To guard against the possibility that these changes might be due to some slow action of the insulating materials of the cathode compartment of the cell on the polysulphide solution, a new polysulphide solution was prepared by shaking freshly made sodium sulphide with sulphur overnight; in the afternoon this solution was divided into two portions, one of which was diluted with its own volume of water and set aside in a glass flask, while the second was diluted in the cell. Table IX gives the results obtained with this second portion; the *LC* of the portion in the flask was determined after 19 hours and found to be 0.44 in good agreement with the final value of the other.

TABLE XI
($\text{Na}_2\text{S}\cdot\text{S}_{29.2}$, 1.92 N)

| | | | | | | | | | |
|--------------------|------|------|------|------|------|------|------|------|------|
| <i>t</i> (minutes) | 7 | 12 | 16 | 22 | 34 | 64 | 242 | 307 | 1082 |
| <i>LC</i> (amp.) | 0.95 | 0.82 | 0.71 | 0.70 | 0.58 | 0.53 | 0.49 | 0.46 | 0.43 |

Something analogous had been noticed with the solution of Table VII ($\text{Na}_2\text{S}\cdot\text{S}_{0.30}$); when the 4.4 N solution was diluted with its own volume of water, the Limiting Current half an hour after dilution was found to be 1.93 amp.; while from an hour and a half to three hours after dilution it stood at 1.63 amp. Nothing similar was observed with the other solutions of Tables VIII and IX; but at the time these measurements were made the possible influence of delay was not suspected, and the Limiting Currents were determined one after the other, (the electrolyte being diluted in the cell) without pause.

(ii) *After heating:* 500 cc. of a solution of the composition $\text{Na}_2\text{S}\cdot\text{S}_{2.79}$, 4.27 N, was heated to boiling with 30 g. of sulphur in a flask provided with a return condenser, and was then kept for four hours at a temperature just below its boiling point. About two-thirds of the sulphur went into solution, and on cooling most of it came out again, the composition of the solution obtained after cooling and filtering being $\text{Na}_2\text{S}\cdot\text{S}_{2.95}$, which means that only 5.5 g. of sulphur had finally been taken up. The solution so prepared was put into the cell, and its Limiting Current was determined; as shown in Table XII, *LC* increased from 0.53 amp. at the time of the first measurement to 1.59 amp. seventeen and a half hours later; during this interval the solution in the cell was kept under an atmosphere of nitrogen as usual.

TABLE XII
($\text{Na}_2\text{S}\cdot\text{S}_{2.95}$, 4.28 N)

| <i>t</i> (minutes after the first <i>LC</i> measurement) | 0 | 30 | 135 | 1050 |
|----------------------------------------------------------|------|------|------|------|
| <i>LC</i> (amp.) | 0.53 | 0.68 | 1.01 | 1.59 |

The solution was then removed from the cell and heated almost to boiling again (this time without adding sulphur) for half an hour; the cell was cleaned, the solution cooled and poured in. Three quarters of an hour after the flask containing the solution had been taken from the hot plate, the Limiting Current was found to be 0.07 amp., which rose to 1.59 amp. twenty-one hours later. (See Table XIII).

TABLE XIII
($\text{Na}_2\text{S}\cdot\text{S}_{4.95}$, 4.28 N)

| <i>t</i> (minutes after the first <i>LC</i> measurement) | 0 | 40 | 70 | 85 | 106 | 148 | 220 | 1255 |
|----------------------------------------------------------|------|------|------|------|------|------|------|------|
| <i>LC</i> (amp.) | 0.07 | 0.28 | 0.64 | 0.65 | 0.66 | 0.70 | 0.96 | 1.59 |

It is well known, of course, that polysulphide solutions turn dark on heating; but when cooled again the dark colour disappears without delay, and nothing like this slow change in a property of the solution after it had been cooled has been recorded. To see whether the change in *LC* was accompanied by a volume change, a solution of the composition of that of Table XII was heated to boiling, and immediately after cooling was introduced into a dilatometer whose bulb held 12 cc. and whose stem had an internal diameter of 0.5 mm.; but no change in volume was noted even after 24 hours.

According to Küster's careful measurements of the solubility of sulphur in sodium monosulphide solutions,¹ the compositions of the saturated solutions change very little indeed with the temperature within the range of his measurements, viz.: from 0°C. to 50°C., and if anything they contain a somewhat smaller proportion of sulphur at the higher temperatures; it is clear from what precedes, that at still higher temperatures the solubility rises considerably. But it is important to note that the 4.27 N solution after depositing most of the sulphur it had dissolved when hot, retained only enough to bring the ratio of sodium to sulphur to that represented by the formula $\text{Na}_2\text{S}_{2.95}$; while Küster's saturated solution of the same normality, obtained by shaking with sulphur at room temperature, had the composition $\text{Na}_2\text{S}_{4.41}$. This observation throws a new light on a remark of Küster's,² viz.:

"It appeared, as was only to be expected, that most of the sulphur was taken up very quickly, whereas complete saturation occurred only after a very long time; and the time the more dilute solutions required for saturation was many times that required for the more concentrated." In a subsequent paper³ he followed the rate of solution by E.M.F. measurements and shewed

¹ Küster: Z. anorg. Chem., 43, 53 (1905).

² Küster: Z. anorg. Chem., 43, 57 (1905).

³ Küster: Z. anorg. Chem., 44, 431 (1905). see p. 433.

that shew "while the 4 N solution of sodium sulphide after a few hours shaking with sulphur appears to be saturated, i.e. its sulphur content remains constant within the experimental error of the gravimetric method of analysis employed, the potential measurements shew that even after 24 hours minute amounts of sulphur are still being taken up, and that true saturation is reached only after 48 hours shaking."

The method used in preparing the solution of Table IX was in effect a solubility determination, and one in which if anything too great a solubility should have been found; for on the one hand the solution analysed was one from which sulphur had just been depositing, and on the other hand, if this sulphur happened to be deposited in a form unstable at room temperature its solubility would have been greater than that of the stable form. Since, on the contrary, this determination gave a much lower value for the solubility than that obtained by Küster, his observation that the last portions of sulphur dissolve very slowly cannot be ascribed (as his "only to be expected" seems to imply) merely to a slow reaction between the solution and the solid, but must be ascribed to an unsuspected change taking place in the solution itself, which rendered it capable of dissolving further quantities of sulphur; and the circumstance that in the freshly cooled solution (before this reaction had time to go very far) the ratio of sodium to sulphur is almost exactly that given by the formula Na_2S_4 , lends further justification to the prominence given by Küster to the tetrasulphide in his discussion of the constitution of the polysulphides.

Summary

(1) Analytical methods are developed for determining the constituents of a solution of sodium sulphide after it has been subjected to electrolysis; and a convenient apparatus for preparing carbonate-free sodium hydroxide solution is described.

(2) When the current density is not too high, the only product of electrolysis is sodium polysulphide; with higher current densities, sulphate and dithionate are formed but no thiosulphate.

(3) When polysulphide is the only product of electrolysis, the electrochemical equivalent of sulphur is 16, whether the electrolyte be sodium monosulphide (Na_2S) or polysulphide.

(4) When a solution of acid sodium sulphide NaSH is electrolysed, polysulphide and hydrogen sulphide are formed in the ratio of Na_2S_2 to $2\text{H}_2\text{S}$.

(5) The Limiting Current, or the current needed to liberate sulphur from a solution of mono- or polysulphide, increases at first with the proportion of polysulphide in the solution, passes through a maximum, and decreases towards zero.

(6) In the case of a solution of sodium monosulphide, the Limiting Current increases with increase in the rate of rotation of the anode, in quantitatively the same proportion as the Limiting Current for an acid solution of copper sulphate.

(7) In the case of polysulphide solutions ($\text{Na}_2\text{S}\cdot\text{S}_{1.01}$ and $\text{Na}_2\text{S}\cdot\text{S}_{1.03}$) the Limiting Current remains unchanged when the rate of rotation is increased

from 220 r.p.m. to 700 r.p.m., while with the monosulphide solution this change doubles the Limiting Current.

(8) Increasing the temperature increases the Limiting Current.

(9) In the case of a monosulphide solution, the Limiting Current is proportional to the concentration; the same is true for polysulphide solutions when the ratio of sulphur to sodium does not exceed that given by the formula Na_2S_3 .

(10) When a polysulphide solution with high sulphur ratio ($\text{Na}_2\text{S}\cdot\text{S}_{2.7}$, $\text{Na}_2\text{S}\cdot\text{S}_{3.0}$) is diluted by adding water, the Limiting Current observed depends upon the time that has elapsed after the water has been added; it is highest at first and falls to a steady value.

(11) When a polysulphide solution is heated and then cooled, its Limiting Current immediately after cooling (but after the solution has regained its original colour) is low, and gradually increases with time, reaching a steady value only after many hours.

(12) When a sulphide solution is cooled after heating with excess of sulphur, much of the sulphur separates; and the solution so obtained retains less sulphur than one that has been shaken with sulphur for a long time at room temperature.

*University of Toronto,
Electrochemical Laboratory,
April, 1928.*

51.5

THE CATALYTIC DECOMPOSITION OF SODIUM HYPOCHLORITE SOLUTIONS*

II. Iron Oxide as Promoter in the Copper Oxide Catalysis of Sodium Hypochlorite

BY JOHN R. LEWIS

In a recent article from this laboratory,¹ it was shown that iron oxide is a promoter in the copper oxide catalysis of sodium hypochlorite solutions. Insufficient data were obtained, however, from which the mechanism of the promoter action could be explained. The data given in this paper are the results that have been obtained in which the promoter effect of iron oxide has been studied more completely. Interesting results have been obtained which tell us something about the mechanism of this particular reaction, and in addition may be of value as a contribution to the broader field of promoter action in heterogeneous catalysis.

The usual definition of promoter action is that given by Rideal and Taylor:² "The beneficial effect produced in a catalyst by admixture with a relatively small quantity of a material, inert or of negligible catalytic activity in the reaction in question." The materials, copper oxide and ferric oxide used as catalyst and promoter in this study fulfill the requirements of the above definition. Copper oxide is a catalyst, ferric oxide is not a catalyst or an extremely poor one. Mixtures of the two, on the other hand, give reaction rates much greater than for the copper oxide used singly.

Experimental

Materials.—The sodium hypochlorite solution was prepared according to the method described in the previous paper. Samples needed for the experiments were withdrawn from the stock supply which was kept in a dark glass container at temperatures below 10°C.

The catalyst solutions were prepared from recrystallized and resublimed chlorides of copper and iron respectively.

Apparatus.—The shaker apparatus,³ described in the previous paper, was used in following the decomposition rate. All the experiments were carried out at 35°C except where temperature coefficients were determined.

* Contribution from the Laboratories of General Chemistry of the University of Wisconsin. Paper read before the Mid-West Regional Meeting of the American Chemical Society, held in Minneapolis, Minn., June 7, 8 and 9 (1928).

¹ J. Phys. Chem., 32, 243-254 (1928).

² "Catalysis in Theory and Practice." By Rideal and Taylor, 2nd. Ed.

³ Walton: Z. physik. Chem., 47, 185 (1904).

Preliminary Experiments.—A series of mixed oxide catalysts containing iron and copper oxide in varying proportions were made by simultaneously precipitating the mixed chloride solutions, using sodium hydroxide as the precipitant. These oxides were washed several times by decantation, and then dialyzed at about 50°C for 50 hours, or until the wash water gave no test for the hydroxyl ion. Finally they were transferred to bottles and made up to definite volumes. The results obtained with these oxides were not reproducible. The factors that were found to affect the reaction rate include the following: age of catalyst, method of its preparation, heat treatments, passing of the oxide suspensions through a colloidal mill, etc. In every case the catalyst became less active. Table I summarizes some of the results obtained using a fixed amount of catalyst and hypochlorite in each case.

TABLE I

| Experiment number | Treatment of catalyst before using | cc. of Oxygen evolved at end of 60 minutes | |
|-------------------|----------------------------------------------------------------------|--------------------------------------------|----------|
| | | Unpromoted | Promoted |
| 1 | Using freshly prepared catalyst | 16 cc. | 35 cc. |
| 2 | Using same catalyst after 7 days | 14.5 cc. | 32 cc. |
| 3 | Passing fresh catalyst through colloid mill 15 times | 13.2 cc. | 30 cc. |
| 4 | Bubbling oxygen through catalyst suspension for 100 hours at 20°C | 12.3 cc. | 27 cc. |
| 5 | Heating freshly prepared catalyst in closed tube at 100°C for 1 hour | 7.6 cc. | 18 cc. |
| 6 | Heating in closed tube at 90°C for 75 hours | .2 cc. | 1.8 cc. |

The following procedure was finally used for obtaining the mixed oxides. Duplications of results, using these catalysts were easily obtained. The error was usually about 2% but in one or two cases it was as high as 5%. A definite volume of ferric chloride and copper chloride solutions was pipetted into the reaction flask, water added and then the mixture transferred to the thermostat until temperature equilibrium had been reached. Finally the desired amount of sodium hypochlorite solution, from a container also at the same temperature was added through the side-neck of the reaction flask.

The free alkali present in the hypochlorite reacted with the mixed chlorides forming the mixed hydrated oxides of copper and iron. The side-neck was closed, the shaker started, the initial reading taken, and then the stop-watch started. This method of preparation of the catalysts furnished a convenient method of following the initial changes in activity of the catalysts.

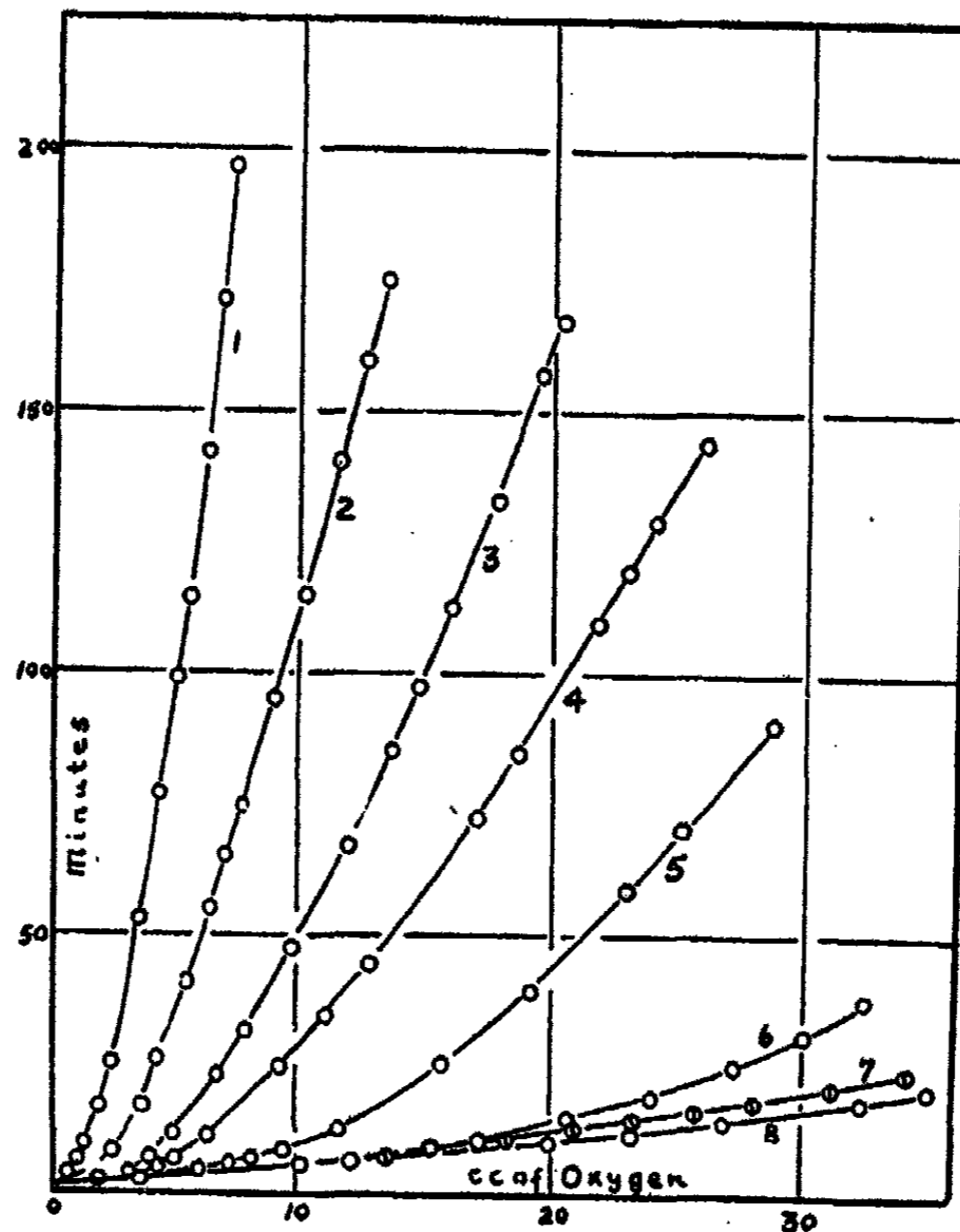


FIG. 1

Curves 1, 2, 3 and 4 are for varying amounts of copper oxide.
Curves 5, 6, 7 and 8 are for varying amounts of iron oxide added to a fixed amount of copper oxide at 35°C.

Results

The results obtained using the procedure described above are given in tables and also presented graphically. The values for K and for K_1 were calculated using the following equations:

$$K = \frac{x}{t} \quad K_1 = \frac{2.303}{t} \log \frac{C_0}{C_0 - C_t}$$

where x is the cubic centimeters of oxygen evolved in time (t) expressed in minutes, and C_0 is the concentration of hypochlorite expressed in cubic centimeters of oxygen at time zero, and C_t is the concentration after time (t).

Table II is for the unpromoted catalyst. Tables III and IV are for the mixed oxides, the former when copper oxide is in excess and the latter when ferric oxide is in excess. In Table V the values for the unpromoted and promoted reaction at various temperatures are given. The data given in Tables II and III are shown graphically in Fig. 1, while the data in Table IV are

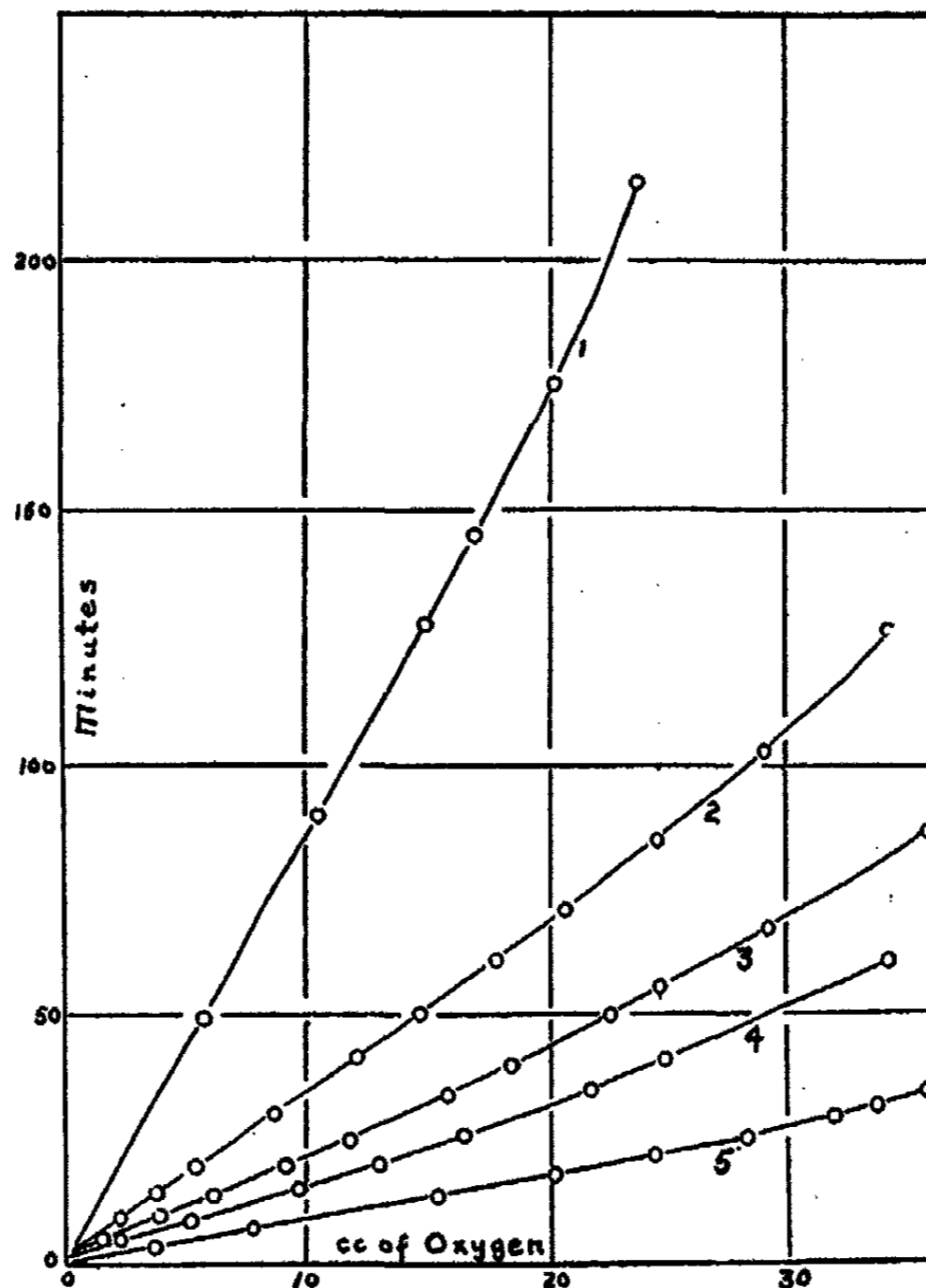


FIG. 2

Increasing amounts of copper oxide added to a fixed excess of iron oxide at 35°C.

shown graphically in Fig. 2. Fig. 3 shows the effect of adding iron oxide to copper oxide and vice-versa. Figs. 4 and 5 present graphically the effect of temperature on the rate of decomposition of the unpromoted and promoted reactions.

These reactions were repeated where the free alkali concentration was considerably higher than in the regular determinations. The rate was slower in every case, but the temperature coefficients were of the same order.

TABLE II

| Temp. 35°C C ₀ = 89.3 | | | | Temp. 35°C C ₀ = 89.3 | | | |
|------------------------------------------|------|------|----------------|-------------------------------------------|------|------|----------------|
| Catalyst: .001494 gr. Cu in 25 cc. | | | | Catalyst: 0.004483 gr. Cu in 25 cc. | | | |
| t | x | K | K ₁ | t | x | K | K ₁ |
| 3 | .73 | .243 | .00304 | 2 | 1.62 | .81 | .00920 |
| 6 | 1.13 | .188 | .230 | 3 | 2.84 | .94 | .1081 |
| 9 | 1.38 | .153 | .206 | 4 | 3.4 | .85 | .00972 |
| 16 | 1.86 | .116 | .144 | 6 | 4.0 | .66 | .766 |
| 25 | 2.3 | .092 | .111 | 11 | 4.95 | .45 | .522 |
| 38 | 2.64 | .069 | .00088 | 23 | 6.73 | .29 | .340 |
| 52 | 3.4 | .065 | .775 | 32 | 7.95 | .24 | .292 |
| 76 | 4.22 | .055 | .65 | 47 | 9.72 | .21 | .245 |
| 98 | 4.87 | .049 | .59 | 69 | 12.0 | .17 | .208 |
| 114 | 5.36 | .047 | .55 | 85 | 13.5 | .16 | .193 |
| 141 | 6.07 | .043 | .51 | 97 | 14.6 | .15 | .183 |
| 171 | 6.8 | .039 | .47 | 112 | 15.9 | .14 | .00175 |
| 196 | 7.36 | .037 | .45 | 132 | 17.6 | .13 | .167 |
| 288 | 9.24 | .032 | .44 | 157 | 19.4 | .125 | .155 |
| 298 | 9.56 | .032 | .38 | 167 | 20.0 | .120 | .151 |
| | | | | 269 | 26.2 | .097 | .133 |

Same as above except 0.002989 gr.
of catalyst used

| | | | |
|-----|-------|------|--------|
| 4 | 1.74 | .434 | .00494 |
| 7 | 2.51 | .369 | .412 |
| 16 | 3.56 | .222 | .255 |
| 26 | 4.22 | .162 | .187 |
| 40 | 5.26 | .131 | .149 |
| 54 | 6.4 | .118 | .137 |
| 64 | 7.17 | .112 | .131 |
| 74 | 7.82 | .105 | .124 |
| 94 | 9.0 | .095 | .112 |
| 114 | 10.12 | .088 | .105 |
| 139 | 11.6 | .083 | .00099 |
| 159 | 12.5 | .078 | .95 |
| 174 | 13.2 | .076 | .92 |
| 276 | 17.2 | .062 | .77 |
| 286 | 17.8 | .061 | .76 |

Same as above except 0.005978 gr.
of catalyst used

| | | | |
|-----|------|------|--------|
| 2 | 2.43 | 1.21 | .01380 |
| 3 | 3.75 | 1.25 | .0144 |
| 4 | 4.3 | 1.07 | .01236 |
| 6 | 5.1 | 0.85 | .00981 |
| 10 | 6.24 | .63 | .00724 |
| 24 | 9.4 | .39 | .462 |
| 34 | 11.2 | .33 | .394 |
| 44 | 12.9 | .27 | .355 |
| 72 | 17.0 | .24 | .294 |
| 84 | 18.7 | .224 | .280 |
| 109 | 21.9 | .205 | .260 |
| 119 | 23.0 | .193 | .250 |
| 129 | 24.0 | .186 | .243 |
| 144 | 25.7 | .179 | .235 |

TABLE III

| Temp. 35°C C _o = 89.3 | | | | Temp. 35°C C _o = 89.3 | | | |
|-----------------------------------------------------------|-------|-------|----------------|-----------------------------------------------------------|------|------|----------------|
| Catalyst: .00578 gr. Cu .000876 gr. Fe in 25 cc. | | | | Catalyst: .005978 gr. Cu .00262 gr. Fe in 25 cc. | | | |
| t | x | K | K ₁ | t | x | K | K ₁ |
| 2 | 3.0 | 1.5 | .01713 | 2 | 2.8 | 1.4 | .01598 |
| 3 | 4.35 | 1.45 | .01664 | 3 | 5.5 | 1.85 | .02125 |
| 4 | 6.13 | 1.53 | .01777 | 4 | 8.2 | 2.05 | .02409 |
| 5 | 7.5 | 1.50 | .01752 | 6 | 12.0 | 2.0 | .02403 |
| 6 | 8.48 | 1.42 | .01659 | 8 | 15.5 | 1.94 | .02381 |
| 8 | 9.75 | 1.220 | .01445 | 10 | 18.3 | 1.83 | .02291 |
| 12 | 11.7 | .976 | .01170 | 12 | 21.0 | 1.75 | .02233 |
| 20 | 13.48 | .675 | .00820 | 14 | 23.4 | 1.67 | .02190 |
| 26 | 15.64 | .602 | .00744 | 16 | 25.8 | 1.61 | .02140 |
| 39 | 19.3 | .495 | .00626 | 18 | 28.1 | 1.56 | .02121 |
| 58 | 23.0 | .396 | .00513 | 21 | 31.2 | 1.48 | .02050 |
| 70 | 25.2 | .360 | .00510 | 24 | 34.1 | 1.42 | .02010 |
| 90 | 28.6 | .318 | .00428 | 29 | 37.9 | 1.31 | .01910 |
| 130 | 34.2 | .263 | .00372 | | | | |

Same as above except 0.001752 gr.
Fe used with 0.005778 gr. Cu

| | | | |
|----|------|------|--------|
| 2 | 2.9 | 1.45 | .01656 |
| 3 | 5.8 | 1.93 | .02238 |
| 4 | 8.4 | 2.1 | .02472 |
| 5 | 10.4 | 2.09 | .02474 |
| 6 | 12.3 | 2.05 | .02468 |
| 7 | 13.6 | 1.95 | .02360 |
| 10 | 17.2 | 1.72 | .02150 |
| 14 | 20.6 | 1.47 | .01880 |
| 19 | 24.1 | 1.27 | .01660 |
| 25 | 27.3 | 1.09 | .01464 |
| 31 | 30.2 | .973 | .01330 |
| 37 | 32.5 | .88 | .01225 |
| 41 | 33.9 | .828 | .01170 |
| 48 | 36.2 | .754 | .01085 |
| 53 | 37.8 | .714 | .01042 |

Same as above except 0.003504 gr.
Fe used with 0.005778 gr. Cu

| | | | |
|----|-------|-------|--------|
| 2 | 2.7 | 1.35 | .01541 |
| 3 | 5.4 | 1.8 | .02077 |
| 4 | 7.7 | 1.92 | .02254 |
| 5 | 10.0 | 2.0 | .02373 |
| 6 | 12.5 | 2.1 | .02528 |
| 7 | 14.56 | 2.08 | .02570 |
| 8 | 16.5 | 2.06 | .02560 |
| 9 | 18.3 | 2.03 | .02560 |
| 10 | 20.2 | 2.02 | .02570 |
| 11 | 21.9 | 1.99 | .0256 |
| 12 | 23.2 | 1.94 | .02522 |
| 14 | 26.8 | 1.915 | .0255 |
| 16 | 30.1 | 1.88 | .0257 |
| 18 | 32.5 | 1.8 | .0252 |
| 20 | 34.9 | 1.75 | .0249 |
| 22 | 38.7 | 1.75 | .0258 |
| 23 | 39.8 | 1.73 | .0257 |

TABLE IV

| Temp. 35°C C ₀ = 89.3 | | | | Temp. 35°C C ₀ = 89.3 | | | |
|-----------------------------------------------|-------|------|----------------|---------------------------------------------|------|------|----------------|
| Catalyst: .00438 gr. Fe .0005978 gr. Cu | | | | Catalyst: .00438 gr. Fe .00239 gr. Cu | | | |
| t | x | K | K ₁ | t | x | K | K ₁ |
| 5 | .43 | .086 | .001012 | 2 | 1.0 | .5 | .00563 |
| 16 | 1.72 | .107 | .1221 | 4 | 2.53 | .63 | .719 |
| 26 | 2.82 | .108 | .1239 | 6 | 3.92 | .65 | .751 |
| 32 | 3.56 | .111 | .1271 | 8 | 5.3 | .66 | .764 |
| 39 | 4.5 | .115 | .1324 | 11 | 7.24 | .66 | .769 |
| 50 | 5.73 | .114 | .1323 | 15 | 9.8 | .65 | .774 |
| 60 | 7.04 | .117 | .1368 | 20 | 13.0 | .65 | .787 |
| 75 | 8.84 | .117 | .1386 | 23 | 14.6 | .635 | .776 |
| 90 | 10.6 | .117 | .1403 | 26 | 16.5 | .634 | .786 |
| 104 | 12.3 | .118 | .1423 | 31 | 19.3 | .624 | .787 |
| 117 | 13.75 | .117 | .1429 | 35 | 21.5 | .614 | .787 |
| 128 | 15.0 | .117 | .1434 | 41 | 24.6 | .60 | .787 |
| 145 | 16.9 | .116 | .1445 | 49 | 28.6 | .585 | .787 |
| 158 | 17.73 | .113 | .1406 | 55 | 31.4 | .572 | .787 |
| 165 | 19.1 | .115 | .1451 | 68 | 37.1 | .546 | .789 |
| 176 | 20.3 | .115 | .1463 | 74 | 40.0 | .542 | .774 |

Same as above except 0.001195 gr.
Cu with 0.00438 gr. Fe

| | | | |
|-----|------|-----|--------|
| 2 | .5 | .25 | .00287 |
| 7 | 1.9 | .27 | .308 |
| 10 | 2.8 | .28 | .320 |
| 15 | 3.9 | .26 | .298 |
| 20 | 5.4 | .27 | .312 |
| 26 | 7.2 | .28 | .324 |
| 31 | 8.7 | .28 | .331 |
| 41 | 12.0 | .29 | .351 |
| 51 | 14.7 | .30 | .353 |
| 61 | 18.3 | .29 | .375 |
| 71 | 20.6 | .29 | .369 |
| 85 | 24.4 | .29 | .375 |
| 98 | 27.6 | .28 | .378 |
| 109 | 30.2 | .28 | .379 |
| 126 | 34.1 | .27 | .381 |
| 146 | 38.4 | .26 | .385 |

Same as above except 0.00478 gr.
Cu with 0.00438 gr. Fe

| | | | |
|----|------|------|--------|
| 2 | 1.4 | .7 | .00749 |
| 3 | 2.92 | .97 | .1110 |
| 4 | 4.7 | 1.18 | .1351 |
| 5 | 6.48 | 1.3 | .1508 |
| 6 | 8.1 | 1.35 | .1582 |
| 8 | 11.2 | 1.4 | .1673 |
| 10 | 14.1 | 1.4 | .1720 |
| 11 | 15.5 | 1.4 | .1732 |
| 13 | 18.3 | 1.4 | .1763 |
| 15 | 20.4 | 1.36 | .1730 |
| 17 | 22.6 | 1.33 | .1715 |
| 19 | 25.0 | 1.32 | .1735 |
| 25 | 32.1 | 1.28 | .1780 |
| 30 | 37.5 | 1.25 | .1814 |
| 32 | 39.6 | 1.24 | .1843 |

TABLE V

| Temp. 25°C C ₀ = 91 | | | | Temp. 25°C C ₀ = 88 | | | |
|-------------------------------------------|------|------|----------------|--------------------------------------------------------------|-------|------|----------------|
| Catalyst: 0.005978 gr. Cu in 25 cc. | | | | Catalyst: 0.005978 gr. Cu 0.003504 gr. Fe in 25 cc. | | | |
| t | x | K | K ₁ | t | x | K | K ₁ |
| 3 | .7 | .23 | .00253 | 3 | 1.3 | .433 | .00498 |
| 5 | 2.5 | .50 | .557 | 5 | 3.11 | .622 | .717 |
| 7 | 4.3 | .614 | .690 | 7 | 5.3 | .75 | .887 |
| 9 | 6.3 | .69 | .796 | 9 | 7.3 | .81 | .961 |
| 11 | 7.4 | .74 | .769 | 13 | 10.3 | .82 | .996 |
| 15 | 9.1 | .60 | .708 | 15 | 12.3 | .82 | .01002 |
| 22 | 10.7 | .486 | .567 | 18 | 14.5 | .81 | .01000 |
| 28 | 11.6 | .414 | .486 | 20 | 15.85 | .794 | .00993 |
| 35 | 12.5 | .357 | .420 | 25 | 19.4 | .777 | .995 |
| 43 | 13.1 | .305 | .361 | 30 | 23.2 | .773 | .01018 |
| 65 | 14.9 | .229 | .274 | 38 | 28.25 | .745 | .01017 |
| 70 | 15.2 | .217 | .260 | 43 | 31.2 | .726 | .01017 |
| Temp. 35°C | | | | 58 | 39.4 | .686 | .01021 |
| 2 | 1.5 | .75 | .00712 | 62 | 41.4 | .668 | .01023 |
| 3 | 3.1 | 1.03 | .01150 | Temp. 45°C | | | |
| 4 | 4.7 | 1.17 | .132 | 1 | 2.6 | 2.6 | .0299 |
| 5 | 6.1 | 1.22 | .1382 | 2 | 6.4 | 3.2 | .0377 |
| 8 | 7.9 | .99 | .1135 | 3 | 10.8 | 3.6 | .0436 |
| 12 | 9.9 | .825 | .00958 | 4 | 14.3 | 3.57 | .0443 |
| 20 | 12.5 | .625 | .735 | 5 | 17.5 | 3.5 | .0449 |
| 30 | 15.0 | .50 | .598 | 6 | 20.8 | 3.47 | .0443 |
| 40 | 17.1 | .427 | .518 | 8 | 26.2 | 3.29 | .0433 |
| 51 | 19.2 | .376 | .463 | 10 | 30.9 | 3.09 | .0425 |
| Temp. 45°C | | | | 12 | 35.2 | 2.94 | .0415 |
| 2 | 2.9 | 1.45 | .01610 | 13.5 | 37.8 | 2.85 | .0412 |
| 4 | 6.3 | 1.57 | .01785 | | | | |
| 8 | 9.1 | 1.14 | .01315 | | | | |
| 10 | 10.3 | 1.03 | .01198 | | | | |
| 16 | 12.7 | .79 | .00936 | | | | |
| 20 | 13.9 | .70 | .827 | | | | |
| 25 | 14.8 | .592 | .00708 | | | | |
| 31 | 16.2 | .523 | .631 | | | | |
| 35 | 16.9 | .483 | .586 | | | | |
| 44 | 18.3 | .416 | .509 | | | | |

Discussion of Results

Examination of the data given in the tables and presented graphically in the figures shows:

1. The reaction is proportional to the concentration of the catalyst.

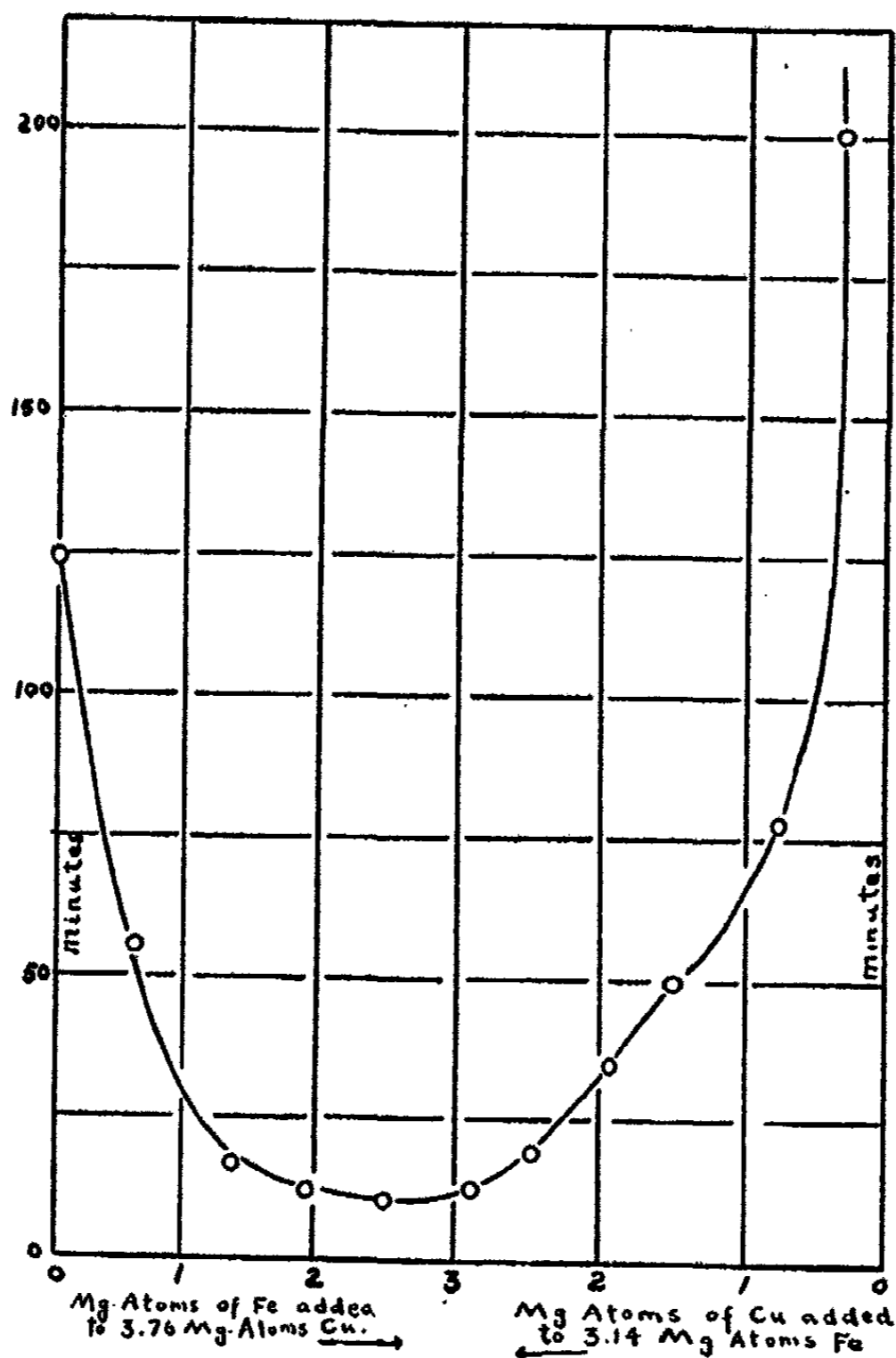


FIG. 3

Points on curve represent time necessary for 25% of the hypochlorite to decompose when CuO and Fe_2O_3 are present in various proportions (35°C).

2. The values for K and K_1 , where the unpromoted catalyst is used, fall off very rapidly after the first 4 or 5 percent of the reaction has been completed.
3. By increasing the amount of promoter for a given quantity of catalyst, the values for K and K_1 fall off less rapidly until (as shown in Table III) satisfactory results for K_1 are obtained.

4. Table IV shows that when small quantities of catalyst are added to an excess of promoter, the values for K are *constant* while K_1 values *increase*.

5. The data shown graphically in Fig. 3 show that the most effective mixture of catalyst and promoter is about one milligram atom of copper to one milligram atom of iron.

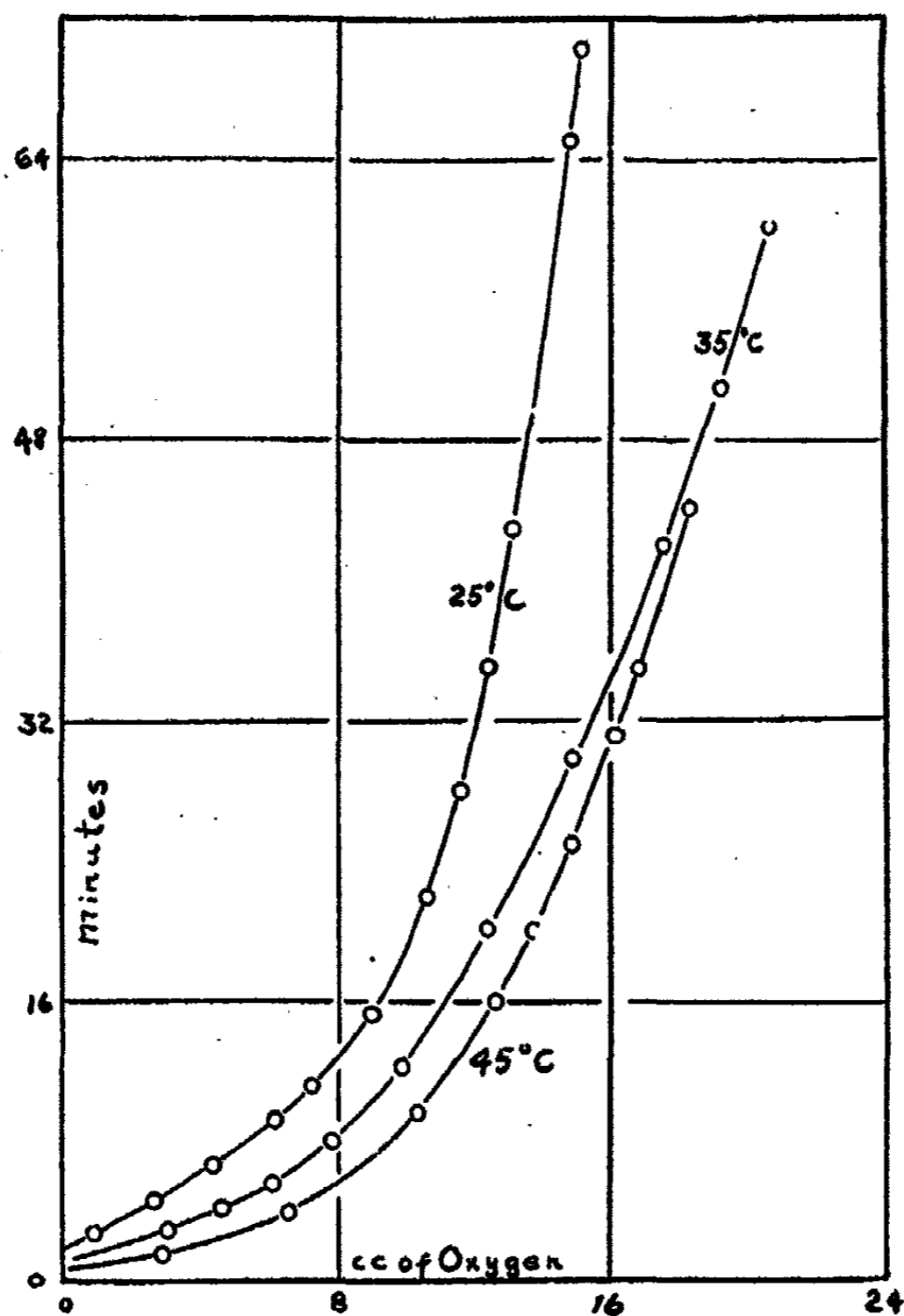


FIG. 4

Copper oxide catalysis of hypochlorite solutions (not promoted) at various temperatures.

6. The temperature coefficient for the unpromoted reaction is low, the values over the temperature range 25°C to 45°C falling between 2.1 and 1.2. The values for the promoted reaction are normal (2.3) over the range 25°C to 35°C but fall off somewhat (1.7) over the range 35°C to 45°C.

The results may be "explained" in the following manner: The reaction is due to the decomposition of a catalyst-hypochlorite complex.¹

¹ J. Phys. Chem., 32, 243-254 (1928).

The reaction takes place at a regular rate as long as the active centers on the catalyst are completely covered with reactant. The initial activity of the catalyst will depend on the method of its preparation and treatment before use. The rapid fall in the reaction rate, (see Table II) using a catalyst prepared by the method described above, is probably due to the changes on the catalyst surface. Coagulation, dehydration, and similar phenomena tend to cut down the number of active points on the catalyst. The low

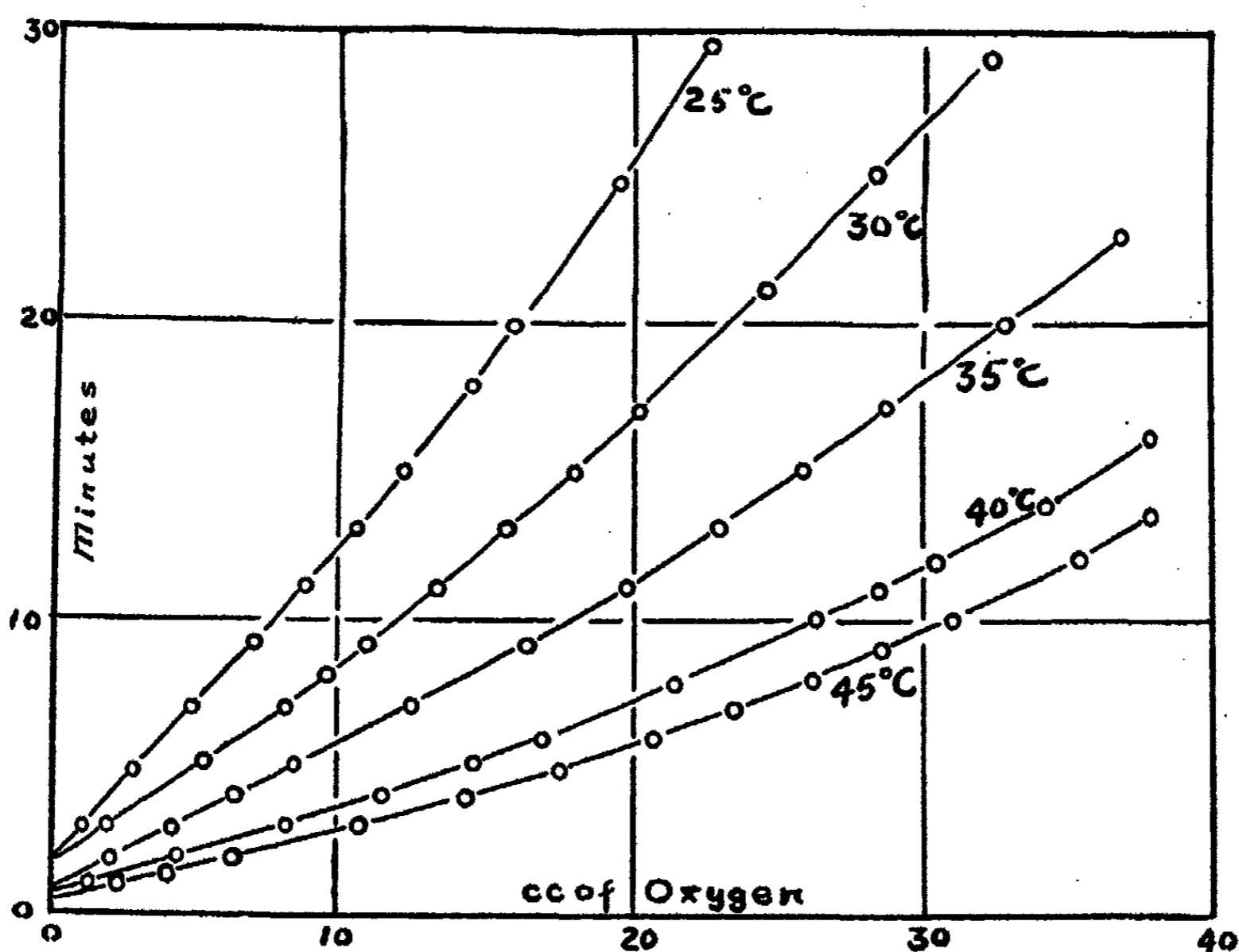


FIG. 5

Iron oxide added to copper oxide to give maximum promotion at various temperatures.

temperature coefficient of the unpromoted reaction may be accounted for by these changes. The normal increase in the reaction rate is offset by the increased rate of decay of active catalyst at the higher temperatures. If the original activity were maintained, the temperature coefficient would be normal.

The function of the promoter is to stabilize the catalyst by preventing the destruction of the active centers. One may think of the promoter as a *support* for the catalyst, for when an excess of promoter is present, all of the initial active centers are preserved over (at least) 20 to 30 percent of the reaction. During that time the reaction takes place at a regular rate. It follows that the promoted reaction should give normal temperature coefficients, at least over a limited temperature range.

The normal temperature coefficient obtained with the promoted reaction suggests the possibility of the reaction taking place in the homogeneous phase. That this is improbable however, may be surmised by the following considerations:

1. The rate of reaction is directly proportional to the concentration of the catalyst present.
2. The rate falls off with certain physical treatments of the catalyst. (see Table I)
3. The catalyst can be poisoned by the addition of certain salts.¹
4. Although sufficient copper and iron are in solution to give positive tests, there is no evidence of decomposition of the hypochlorite unless the oxides are present.

Summary

1. The promoter effects of iron oxide on the copper oxide catalysis of sodium hypochlorite solutions has been studied. The data obtained are given in tables and shown graphically in figures.
2. It was shown that the function of the promoter, in this particular case, is to preserve the active points on the catalyst.

This work is being continued, using other promoters and catalysts.

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¹ Unpublished results obtained in this laboratory.

6-690
THE "SALT ERROR" OF INDICATORS IN THE COLORIMETRIC
DETERMINATION OF pH*

BY I. M. KOLTHOFF

1. Introduction

It is a well known fact that the color of an indicator in two solutions having the same pH but containing different amounts of electrolytes is usually not the same. Indicators with an acidic character show in the solution with the highest salt content a too alkaline reaction, whereas basic indicators adopt a more alkaline tint than corresponds to that in solutions with a smaller electrolyte content at the same pH. In his pioneer work on the determination and significance of pH, S. P. L. Sørensen¹ was already aware of this salt error of indicators and determined the salt correction for different dyestuffs. After him several other workers made more or less detailed experimental studies on this subject.²

For several reasons it is very hard to give a systematic treatment of the salt error of indicators. The latter is not only dependent upon the salt content of the buffer mixture used for comparison, but also on the specific character of the indicator, the kind and valence of the cations present and to a lesser degree on the type and valence of the anions.

In his excellent monograph on indicators, N. Bjerrum³ made the first attempt to give a theoretical explanation of the salt error. Accepting the theory of Sv. Arrhenius on the dissociation of electrolytes and assuming that the undissociated indicator salt has the same color as the indicator ions, it is readily understood that electrolytes will affect the color as they change the degree of dissociation of the indicator salt and therefore change the equilibrium between the acid and alkaline form even if the pH is not changed. According to the modern theory of the strong electrolytes we may interpret the influence of salts by the fact that they change the activity coefficient of the different forms of the indicator.⁴

Let us consider a monovalent indicator acid the color of which is governed by the ratio, undissociated indicator acid to indicator salt. At a definite hydrogen ion concentration the following equation holds:

$$\frac{f_0 [\text{HI}]}{f_1 [\text{I}^-]} = \frac{[\text{aH}^+]}{K_1} \quad (1)$$

* Contribution from the School of Chemistry, University of Minnesota.

¹ S. P. L. Sørensen: *Compt. rend. Lab. Carlsberg*, 8 (1909); *Biochem. Z.*, 21, 159 (1909).

² For literature review, compare W. M. Clark: "The Determination of Hydrogen Ions," 2nd edition (1922); I. M. Kolthoff: "The Use of Indicators" (1926).

³ N. Bjerrum: "Theorie der alkalimetrischen und azidimetrischen Titrierungen," Sonderausgabe aus der Sammlung chemisch und chemisch-technischer Vorträge (1914).

⁴ Compare J. N. Brønsted: *J. Chem. Soc.*, 119, 574 (1921).

f_0 represents the activity coefficient of the undissociated acid, f_1 the same of the indicator salt, a_{H^+} the activity of the hydrogen ions, and K_1 the dissociation constant of the indicator. From equation (1) it follows that the color of a monobasic indicator acid is governed by the equation:

$$\frac{[HI]}{[I^-]} = \frac{[a_{H^+}] f_1}{K_1 f_0} \quad (2)$$

In agreement with the studies of Sv. Arrhenius¹, Bjerrum assumed that neutral salts not only change the degree of dissociation of the indicator salt but also increase the dissociation constant K_1 . According to the modern views this assumption does not seem to be correct. Previous authors did not take into account the fact that the activity coefficient f_0 of the undissociated acid usually increases on the addition of neutral salts.² So far this change of f_0 with varying electrolyte content cannot be calculated, though P. Debye and McAuley³ derived a mathematical expression for it. From studies on the influence of neutral salts on the equilibrium between weak acids and their salts I. M. Kolthoff and W. Bosch⁴ concluded that neutral salts do not affect the dissociation constant of an acid if the change of f_0 is accounted for.

If we add the same amount of a monovalent indicator acid to two solutions having the same pH but containing different amounts of electrolytes, then the ratio of (HI) and (I⁻) in both liquids will be different. Equation (1) shows that

$$\frac{f_0' [HI_1]}{f_1' [I_1^-]} = \frac{f_0'' [HI_{II}]}{f_1'' [I_{II}^-]} \quad (3)$$

From equations (2) and (3) we find that the difference in color between the two solutions will correspond to a difference in pH:

$$\Delta pH = + \left(\log \frac{f_0'}{f_1'} - \log \frac{f_0''}{f_1''} \right)$$

A similar expression can be derived for a divalent indicator acid, the monovalent ions of which show the acid, and the divalent ions the alkaline color (for example the sulphophthaleins):

$$\Delta pH = + \left(\log \frac{f_1'}{f_2'} - \log \frac{f_1''}{f_2''} \right)$$

f_1 representing the activity coefficient of the monovalent anions and f_2 the same for the divalent ions.

As the ratio f_1 to f_2 increases much more with increasing ionic strength than that of f_0 to f_1 , the salt error of divalent indicator acids will be much larger than that of monovalent indicators. In solutions with not too large a salt content the equation of Debye and Hückel holds:

¹ Sv. Arrhenius: Z. physik. Chem., 31, 197 (1899).

² Compare the review by Merle Randall and C. F. Failey: Chem. Rev., 4, 271, 285, 291 (1927).

³ Debye and McAuley: Physik Z., 26, 22 (1925); Debye: Z. physik. Chem., 130, 56 (1927).

⁴ Kolthoff and Bosch: Rec. Trav. chim., 47, 558 (1928).

$$-\log f = \frac{.5 z^2 \sqrt{\mu}}{1 + .329 \times a \times 10^8 \sqrt{\mu}} \quad (18^\circ)$$

z represents the valence of the anion under consideration, μ the total ionic strength and a the size of the ions. If we assume that for all the monovalent indicator acids f_0 is the same at the same ionic strength of the solution, then the monovalent indicator acids should have the same salt error. By means of the equation of Debye and Hückel we derive for a divalent indicator acid the relation:

$$-\log \frac{f_1}{f_2} = \frac{1.5 \sqrt{\mu}}{1 + .329 \times a \times 10^8 \sqrt{\mu}}$$

On this basis we can expect that the dibasic indicators have the same salt error under the same conditions. The size of the ions in the solution and the ionic strength mainly determine the salt error. An indicator will show a different salt error in two solutions having the same pH and ionic strength but a different size of ions. At smaller salt content ($\mu < .05$) the difference in ionic size will be practically negligible and therefore we might expect that the salt error of indicators of the same basicity will be the same at small ionic strength. As a matter of fact the salt error observed will also depend upon the ionic strength of and the size of the ions in the buffer mixture used for comparison. The sign of the salt error (or the salt correction) will change at the ionic strength of the buffer mixture. In reporting work on the salt error of indicators the ionic strength and the composition of the buffer mixtures used for comparison should be mentioned.

By means of the equations of Debye and Hückel we are able to calculate the salt error of the different indicators at varying ionic strength. However, there are different reasons why the values calculated in this way do not agree exactly with the experimental data; especially at high ionic strengths. There seems to exist a specific interaction between cations and anions¹ which may result in a kind of association of ions in the sense of N. Bjerrum.² Moreover, we are not sure whether the indicator salts behave as ideal, strong electrolytes; it is possible that they are not completely dissociated into the ions especially at larger salt contents. Another factor we must consider is the possible influence of the electrolytes on the equilibrium between the pseudo and true acid form of the indicator. A shift of this equilibrium causes a change of the dissociation constant of the indicator. Finally the excellent investigations of H. v. Halban and L. Ebert³ show very distinctly that neutral salts may change the value of the extinction coefficient of one or both of the indicator forms to a considerable amount. In order to account quantitatively for this effect, the extinction coefficient of the indicators in acid and alkaline medium should be determined at different salt contents. Theoretically this point is very interesting; for practical application it has less significance. The ordinary colorimetric measurement of pH is done without a spectrophoto-

¹ Compare J. N. Brønsted: *Trans. Faraday Soc.*, **77**, 416 (1927).

² N. Bjerrum: *Det. Danske Videnskabernes Selskab.*, **7**, (1926).

³ H. v. Halban and Ebert: *Z. physik. Chem.*, **112**, 321, 359 (1924).

meter and the colors are observed in daylight (or special artificial light). Therefore the salt effect has to be determined in a similar way. From colorimetric measurements, I found that neither the acid nor the alkaline colors of dilute solutions of bromphenolblue, bromcresolgreen, bromthymolblue, phenolred, cresolred, and thymolblue are affected by large amounts of salts; on the other hand the acid color of methylorange, tropaolin oo and methylred in the presence of salts is more intense than in solutions with a low salt content, whereas the color of the alkaline form of the different nitrophenols and salicylyellow is more intense at higher salt content.

For all these reasons it is very hard to give a general theoretical treatment of the salt error, which takes into account all the different factors which may influence it. Especially at higher salt concentrations individual differences between the different indicators may be expected, whereas at small ionic strengths of the solutions a more uniform behavior of indicators of the same basicity may be expected.

2. Experimental

The colorimetric readings were made in the ordinary way, Jena or Pyrex test tubes of the same size and diameter being used. All solutions were measured with the hydrogen electrode at 18°, and their values accepted as standards. The relative error of a colorimetric determination is rather large; though the average of three to four independent readings were taken, the experimental uncertainty amounts to about $\pm .02$ pH.

In the following tables the results are given. The first column of Table I gives the composition of the solution used, the second its ionic strength, the third the pH as measured with the hydrogen electrode, the fourth the pH found in a colorimetric way, and the last the salt correction of the special indicator. In the different cases the types of buffer solutions used for comparison are mentioned.

Methylorange: 0.1 c.c. of 0.1% solution in water was added to 7 c.c. solution. As the biphthalate mixtures of Clark and Lubs exercise a specific influence upon the color of methylorange¹ citrate buffer solutions according to Kolthoff and Vleeschhouwer² were used for comparison. The ionic strength of the buffers used was approximately .05.

TABLE I
Salt correction of methylorange in citrate solution

| Concentration Mono- potassium citrate | μ | pH electrom. | pH color. | Salt corr. Methylorange |
|------------------------------------------|-------|--------------|-----------|----------------------------|
| .25 molar | .25 | 3.59 | 3.57 | + .02 |
| .1 " | .1 | 3.67 | 3.70 | - .03 |
| .05 " | .05 | 3.73 | 3.75 | - .02 |
| .01 " | .01 | 3.83 | 3.85 | - .02 |
| .002 " | .002 | 3.91 | 3.95 | - .04 |
| .001 " | .001 | 3.96 | 4.00 | - .04 |

¹ Compare I. M. Kolthoff: *Rec. Trav. chim.*, 45, 433 (1926).

² *Biochem. Z.*, 179, 410 (1926); 183, 444 (1927).

The pH of monopotassium citrate at different concentrations was measured. Methylorange has practically no salt error at all, and therefore it is an ideal indicator for colorimetric measurements of pH.

β Dinitrophenol: 0.2 c.c. of a 0.05% solution of the indicator was added to 7 c.c. liquid. The colorimetric readings were not very sharp.

*Hexamethoxytriphenylcarbinol:*¹ 0.1 c.c. of 0.1% alcohol solution of indicator was added to 7 c.c. of liquid.

Bromphenolblue: 0.1 c.c. of 0.1% solution of the indicator neutralized according to Clark was used. The results obtained with the different indicators are combined in Table II. As the composition of the solution was the same as in Table I, we report only the salt corrections of the respective indicators.

TABLE II
Salt correction of *β* dinitrophenol, hexamethoxytriphenylcarbinol and bromphenolblue

| Concentration Mono- potassium citrate | μ | <i>β</i> dinitrophenol | hexamethoxyred | bromphenol-blue |
|------------------------------------------|-------|------------------------|----------------|-----------------|
| .25 molar | .25 | -.51 | +.19 | -.13 |
| .1 " | .1 | -.08 | +.12 | -.07 |
| .05 " | .05 | -.07 | +.03 | -.02 |
| .01 " | .01 | -.02 | -.07 | +.05 |
| .002 " | .002 | +.01 | -.04 | +.07 |
| .001 " | .001 | +.09 | -.05 | +.06 |

As may be expected the salt error of hexamethoxytriphenylcarbinol has the opposite sign from that of the two other indicators, because the former has basic properties whereas the two others are weak acids. The salt correction of *β* dinitrophenol in the stronger citrate solutions is abnormally large. L. Michaelis² and collaborators also found an appreciable error in solutions containing large amounts of neutral salts. Therefore the *β* dinitrophenol is not very useful as an indicator for exact colorimetric measurements. In .05 molar monopotassium citrate solution the ionic strength is about the same as that in the buffer mixtures used. In agreement we find at that concentration the salt correction for hexamethoxyred and bromphenolblue practically equal to zero, whereas the correction changes its sign at that ionic strength.

In the following experiments the pH was measured in an equimolecular mixture of mono- and dipotassium citrate and its successive dilutions. The original solution was .167 molar with respect to mono- and dipotassium salt respectively; it was .5 N with respect to potassium, and the ionic strength equal to .667. In order to measure the influence of some neutral salts a very dilute citrate mixture with an ionic strength of .0133 was taken and the pH measured in the presence of .5 N solutions of some neutral salts.

¹ Compare I. M. Kolthoff: J. Am. Chem. Soc., 49, 1218; H. Lund: 1346 (1927).

² L. Michaelis and A. Gyemant: Biochem. Z., 100, 165 (1920); Michaelis and Krüger: 119, 307 (1921).

Sodium Alizarinsulphonate: .1 c.c. of a 1% solution of the indicator in water was added to 7 c.c. of liquid. Citrate buffer mixtures were used for comparison. The ionic strength of the buffer at pH 4.2 is equal to .057, at 4.4 to .065, and at 4.5 to .070.

The first column in Table III gives the analytical normality of the solution. Column 2 gives its ionic strength and column 3, the pH measured with the hydrogen electrode.

TABLE III

Salt correction of alizarinsulphonate in citrate solutions and in the presence of neutral salts

| Normality citrate solution | μ | pH electrom. | pH color. | Salt correction |
|-----------------------------|-------|--------------|-----------|-----------------|
| .5 | .667 | 4.29 | 4.55 | -.26 |
| .1 | .133 | 4.40 | 4.52 | -.12 |
| .05 | .0667 | 4.48 | 4.48 | .00 |
| .025 | .0333 | 4.53 | 4.50 | +.03 |
| .01 | .0133 | 4.60 | 4.48 | +.12 |
| .005 | .0067 | 4.63 | 4.52 | +.11 |
| .0025 | .0033 | 4.65 | 4.50 | +.15 |
| .01 + .5 N KCl | .51 | 4.20 | 4.55 | -.35 |
| .01 + .5 N NaCl | .51 | 4.07 | 4.50 | -.43 |
| .01 + .5 N KNO ₃ | .51 | 4.21 | 4.55 | -.34 |

TABLE IV

Salt correction of bromchlorphenolblue, bromphenolblue, bromcresolgreen and α dinitrophenol in citrate solutions and in the presence of neutral salts

| Normality citrate solutions | μ | Salt correction of | | | |
|-----------------------------|-------|-----------------------|-----------------|------------------|-------------------------|
| | | chlorbrom-phenol blue | bromphenol-blue | bromcresol-green | α dinitro-phenol |
| .5 | .667 | -.13 | -.11 | -.04 | -.15 |
| .1 | .133 | -.02 | -.10 | -.05 | |
| .05 | .067 | .00 | .00 | +.01 | |
| .025 | .033 | +.03 | +.03 | .00 | .00 |
| .01 | .013 | +.10 | +.08 | +.10 | |
| .005 | .0067 | +.15 | +.08 | +.10 | +.17 |
| .0025 | .0033 | +.20 | +.07 | +.15 | |
| .01 + .5 N KCl | .51 | -.18 | -.15 | -.17 | -.15 |
| .01 + .5 N NaCl | .51 | -.23 | -.23 | -.21 | -.23 |
| .01 + .5 N KNO ₃ | .51 | -.14 | -.14 | -.11 | |
| .01 + .5 N KI | .51 | -.12 | -.12 | -.08 | |

In Table IV the results obtained with bromchlorphenolblue (unneutralized solution), bromphenolblue, bromcresolgreen, and α dinitrophenol are reported. In the latter case the colorimetric readings were not very sharp. The solutions used had the same composition as those in Table III. For this reason we only give the salt corrections of the different indicators.

The salt error of alizarinsulphonate is rather high, at large as well as at small salt concentrations, therefore, this indicator is not very suitable for accurate pH work. At the point where the ionic strength of the solution is the same as that of the buffer used for comparison, the sign of correction reverses again. In agreement with the data found with other indicators (Compare Table IV and others), the salt error in the presence of neutral salts is larger than that with citrate alone at the same ionic strength. Moreover, there seems to be a cation effect, the salt error in the presence of sodium salts being larger than with potassium salts under the same conditions.

Considering the results of Table IV, we find that α dinitrophenol has a considerable salt error, the values being more or less in agreement with those of Michaelis and Krüger. The three sulphonphthaleins in the presence of .5 N neutral salts have approximately the same salt error. In citrate solutions of the same ionic strength this salt correction is considerably lower. This conclusion can also be drawn from the experimental work of Barnett Cohen.¹ At small ionic strength the salt error of bromchlorphenolblue especially seems to be appreciable. In agreement with the results given in Table II, the correction for bromphenolblue in solutions with a low salt content is very small. So far, however, it is hard to make an exact comparison between the correction of the different indicators in solutions with a poor buffer action as the purity and the right neutralization of the indicator may have a noticeable influence.

The salt error of Congo red is not reported in the table. The corrections under different conditions are so high that the indicator is useless for colorimetric work.

In Table V the salt correction of methylred is reported. The pH was measured of an equimolecular mixture of di- and tri-potassium citrate and

TABLE V
Salt correction of methylred in citrate solutions and in the presence of neutral salts

| Normality citrate solution | μ | pH electrom. | pH color | Correction |
|-----------------------------|-------|--------------|----------|------------|
| .5 | .9 | 5.61 | 5.57 | + .04 |
| .1 | .18 | 5.81 | 5.84 | - .03 |
| .05 | .090 | 5.91 | 5.94 | - .03 |
| .025 | .045 | 6.01 | 6.02 | - .01 |
| .01 | .018 | 6.12 | 6.10 | + .02 |
| .005 | .009 | 6.17 | 6.15 | - .02 |
| .01 + .5 N KCl | .52 | 5.47 | 5.42 | + .05 |
| .01 + .5 N NaCl | .52 | 5.29 | 5.37 | - .08 |
| .01 + .5 N KI | .52 | 5.48 | 5.35 | + .13 |
| .01 + .5 N KNO ₃ | .52 | 5.53 | 5.45 | + .08 |

¹ Cohen: Public Health Reports, 42, 3051 (1927); reprint No. 1131, compare especially p. 21.

its successive dilutions. The original solution was .1 molar with respect to both salts, or .5 normal with respect to potassium; its ionic strength was .9. In order to measure the influence of neutral salts, the latter were added to the citrate mixture with an ionic strength of .018.

Clark's biphthalate-sodiumhydroxide buffer solutions were used for comparison. The ionic strength in a mixture with a pH of 5.6 is .13, and with a pH of 6.0, .14.

From these figures it appears that under different conditions the salt error of methylred usually is negligibly small. Therefore it is an ideal indicator for the colorimetric measurement of pH.

In Table VI the salt corrections for chlorphenolred, bromcresolpurple and p-nitrophenol are mentioned. The same citrate solutions were used as in the case with methylred. The two sulphonphthaleins were neutralized according to Clark's procedure.

TABLE VI
Salt correction of chlorphenolred, bromcresolpurple and p-nitrophenol in citrate solutions and in the presence of neutral salts

| Normality citrate solution | μ | Chlorphenol-red | Bromcresol-purple | Salt Correction of p-Nitrophenol |
|-----------------------------|-------|-----------------|-------------------|----------------------------------|
| .5 | .9 | -.06 | -.21 | +.06 |
| .1 | .18 | -.02 | -.05 | -.03 |
| .05 | .090 | +.03 | +.03 | +.01 |
| .025 | .045 | +.09 | +.09 | +.03 |
| .01 | .018 | +.15 | +.17 | +.02 |
| .005 | .009 | +.17 | +.17 | .00 |
| .0025 | .0045 | +.18 | +.18 | +.05 |
| .01 + .5 N KCl | .52 | -.11 | -.23 | -.13 |
| .01 + .5 N NaCl | .52 | -.16 | -.31 | -.16 |
| .01 + .5 N KI | .52 | -.09 | -.22 | |
| .01 + .5 N KNO ₃ | .52 | -.04 | -.17 | -.12 |

In the most concentrated citrate mixture an abnormal value for the salt error of p-nitrophenol has been found. Probably there is some specific action between p-nitrophenol and citrate. In .5 N neutral salt solutions normal values are found, the correction measured in .5 N sodium chloride is exactly the same as that given by S. P. L. Sørensen and S. Palitzsch.¹

At an ionic strength smaller than .15 the salt error of p-nitrophenol is negligibly small. The salt error of chlorphenolred in the more concentrated citrate solutions is also exceptionally small. Even in the presence of neutral salts the correction is much smaller than that for bromcresolpurple. In .5 N sodium chloride B. Cohen found a correction of -.20, whereas our value in the table is -.16. In solutions with an ionic strength smaller than .15 chlorphenolred and bromcresolpurple show the same error.

¹ Sørensen and Palitzsch: Compt. rend. Lab. Carlsberg, 10, 1228 (1913).

In Table VII the salt corrections for bromthymolblue, phenolred and neutralred are reported. The measurements were made with neutralized and unneutralized sulphophthaleins, no differences being observed. A phosphate buffer solution with a pH of 7.0 according to Clark was prepared, and the pH of its successive dilutions measured. The undiluted mixture had an ionic strength of .11. The influence of neutral salts was measured by adding the latter to a phosphate dilution with an ionic strength of .022. Phosphate buffer solutions according to Clark were used for comparison.

TABLE VII
Salt correction of bromthymolblue, phenolred and neutralred

| Phosphate mixture Clark | μ | pH electrom. | bromthy- molblue | phenol- red | neutral- red |
|----------------------------|-------|--------------|---------------------|----------------|-----------------|
| 2 X diluted | .055 | 7.06 | +.04 | +.02 | -.02 |
| 5 X " | .022 | 7.14 | +.07 | +.08 | -.04 |
| 10 X " | .011 | 7.17 | +.11 | +.11 | -.05 |
| 20 X " | .0055 | 7.18 | +.12 | +.13 | -.06 |
| 50 X " | .0022 | 7.19 | +.14 | +.14 | -.06 |
| 5 X dil. + .25 N KCl | .27 | 6.78 | -.17 | -.17 | |
| " + .5 N KCl | .52 | 6.68 | -.20 | -.20 | +.07 |
| " + .5 N KBr | .52 | 6.64 | -.20 | -.21 | +.13 |
| " + .5 N KI | .52 | 6.63 | -.20 | -.19 | |
| " + .25 N NaCl | .27 | 6.70 | -.19 | -.20 | +.05 |
| " + .5 N NaCl | .52 | 6.53 | -.28 | -.29 | |

Bromthymolblue and phenolred have the same salt correction under the same conditions. As in all former cases we find a larger salt error with sodium chloride than with the same concentration of potassium salt. At a small ionic strength of the solution the salt correction for neutralred is very slight.¹ Therefore it is preferable to phenolred for the measurement of pH with a small electrolyte content, e.g. in tapwater. Formally I found in the city water of Utrecht (ionic strength about .0015) a pH with neutralred of 7.47, with neutralized phenolred 7.23 (unneutralized 7.15). The most probable value of the pH is therefore 7.4.

TABLE VIII
Salt correction of phenolphthalein and thymolblue in borax solutions

| Concentration borax | μ | pH electrom. (18°) | phenolphthalein | thymolblue |
|------------------------|-------|-----------------------|-----------------|------------|
| .25 molar | .5 | 9.30 | -.24 | -.22 |
| .1 " | .2 | 9.27 | -.07 | -.05 |
| .05 " | .1 | 9.22 | -.05 | -.03 |
| .01 " | .02 | 9.20 | +.06 | +.05 |
| .005 " | .01 | 9.19 | +.08 | +.08 |
| .0025 " | .005 | 9.20 | +.14 | +.11 |

¹ Comp. are also J. T. Saunders: Proc. Cambridge Phil. Soc., 1, 30 (1923).

In solutions with a large excess of neutral salt the neutralred is not very useful, as the salts intensify the color depth of the acid form considerably.

In Table VIII the salt corrections of phenolphthalein and thymolblue are given. The measurements have been made in .25 molar borax solution and its successive dilutions.

Clark's boric acid (+ potassium chloride)—sodium hydroxide buffer mixtures were used for comparison. The ionic strength of these buffers is at pH 9.0, .071, at 9.2, .077, at 9.4, .082 and at 9.6, .087. Our values are in fairly good agreement with those reported in the literature (Compare Sørensen and Palitzsch, and Saunders).

In the following table the salt correction of thymolphthalein is given. .1 c.c. of .1% solution in 70% alcohol was added to 7 c.c. liquid. The pH of an equimolecular mixture of .25 molar mono- and .25 molar disodium carbonate and its successive dilutions was measured. The original solution had an ionic strength of 1.0. It should be mentioned, however, that measurements made at this high salt concentration are wrong, due to the fact that a part of the thymolphthalein is flocculated. The indicator is very slightly soluble in water. If the measurements are repeated with .05 c.c. of indicator instead of .1 c.c., better values are obtained, but they still are in error. In the presence of .5 N potassium chloride the effect is much less than in the stronger carbonate containing solutions. Quite generally it is often observed, that the color of thymolphthalein in a solution fades on standing. Probably the reason again is that a small part of the indicator separates out, and the reaction observed is too acid. For comparison freshly prepared mixtures of sodium carbonate and borax were used. They had an ionic strength of .128 at pH 9.6, of .133 at pH 9.8, and .138 at pH of 10.0.

TABLE IX

Salt correction of thymolphthalein in sodium bicarbonate—carbonate solutions and in the presence of neutral salts

| Ionic strength carbonate solution | pH electrom. (18°) | pH color. | Salt correction |
|-----------------------------------|--------------------|-----------|-----------------|
| 1.0 | 9.65 | (9.5) | (+.15) |
| .5 | 9.77 | (9.7) | (+.07) |
| .2 | 9.87 | 9.9 | -.03 |
| .1 | 9.94 | 9.92 | +.04 |
| .05 | 10.02 | 9.98 | +.04 |
| .02 | 10.08 | 9.96 | +.12 |
| .01 | 10.10 | 9.96 | +.14 |
| .02 + .1 N KCl | 9.89 | 9.90 | -.01 |
| .02 + .5 N KCl | 9.68 | 9.84 | -.16 |

In Table X, the salt corrections of alizarinyellow and salicylyellow are reported. The same solutions and type of buffer mixtures were used as for the experiments in the previous table.

TABLE X

Salt error of alizarinyellow and salicylyellow in sodium bicarbonate—carbonate solution and in the presence of neutral salts

| Ionic strength carbonate mixture | alizarinyellow | Salt correction of salicylyellow |
|----------------------------------|----------------|----------------------------------|
| 1.0 | -.43 | -.40 |
| .5 | -.28 | -.26 |
| .2 | -.19 | -.18 |
| .1 | -.10 | -.16 |
| .05 | -.02 | -.06 |
| .02 | +.02 | +.03 |
| .01 | +.10 | +.06 |
| .02 + .1 N KCl | -.16 | |
| .02 + .5 N KCl | -.57 | -.52 |
| .02 + .5 N NaCl | -.58 | -.54 |

The salt error of both indicators at higher salt concentrations is very large: for this reason they cannot be recommended for accurate colorimetric measurements of pH

Even in the case where the ionic strength of the solution is the same as that in the buffer mixture there is a distinct deviation from the true value. This is probably due to the fact that the buffer mixture contained boric acid, and it seems that the latter has a distinct effect on the color of the acid form of the indicators.

3. Discussion of Results

Of practical as well as of theoretical interest is the fact, that methylorange and methylred have practically no salt error or a very slight one at the electrolyte concentrations used. This specific behavior has to be attributed to their hybrid character. The acid (red) form of both indicators behaves as a hybridion (Zwitterion) + R⁻

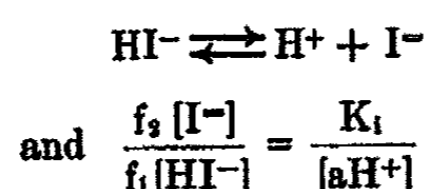


$$\frac{f_1 \overset{\text{red}}{[+R^-]} [aOH^-]}{f_2 [R^-]} = K_b \text{ or } \overset{\text{yellow}}{[R^-]}$$

$$\frac{f_1 [+R^-]}{f_2 [R^-]} = \frac{K_b}{K_w} [aH^+]$$

f_1 is the activity coefficient of the hybridion, f_2 the same of its anions. If both activity coefficients on the addition of an electrolyte change to the same extent, the indicator would show no salt error. Approximately, this seems to be the case here. From the practical point of view it would be very important to have indicators with hybrid character available over the whole range of

pH between 2 and 12, because it may be expected that their salt error will be very small and therefore they will be useful for the accurate determination of the acidity under different conditions. Tropaeolin oo (color change between pH 1.3 and 3.0) for example is such a type of indicator and therefore it has a negligibly small salt error. The other indicators, which behave as mono- or polyvalent acids or bases respectively show pronounced salt errors. It is interesting to compare the salt error of the different sulphonphthaleins and phthaleins at the same ionic strength of the solution. In order to obtain comparable results we have to relate all the values to the same ionic strength of the buffer solution, for which we have taken a value of .1. The buffer mixtures used in the different experiments had an ionic strength between .07 and .14. The color change of the sulphonphthaleins is governed by the equation:



If we work with solutions with an ionic strength smaller than that of the buffer mixture, and if the latter has an ionic strength of .07, the salt correction will be smaller than in the case where the buffer has an ionic strength of .1. In order to relate the salt error to an ionic strength of the buffer equal to .1 we have to add a small value to the salt correction found. This additional factor is equal to the difference between $-\log f_2/f_1$ in the buffer at μ equal to .1 and .07. It can be calculated by means of the Debye and Hückel equation:

$$-\log \frac{f_2}{f_1} = \frac{1.5\sqrt{\mu}}{1 + .329 \times a \times 10^8 \sqrt{\mu}}$$

The exact value of a is, in our case, of minor importance, as the ionic strength of the buffer mixtures used does not differ very much from .1. For the calculations I accepted a value for the ionic size of 4×10^{-8} ; practically the same corrections are found with a value of a of 6×10^{-8} .

TABLE XI

Salt correction of the different phthaleins at low electrolyte content of the solution as compared with buffer mixtures with an ionic strength of .1

| Ionic strength solution | B.P.B. | B.C.G. | B.C.P. | C.P.R. | B.T.B. | P.R. | Phpt. | T.B. | Thpt. |
|-------------------------|--------|--------|--------|--------|--------|------|-------|------|-------|
| .02 | + .13 | .14 | .14 | .12 | .08 | .07 | .10 | .09 | .09 |
| .01 | .14 | .16 | .13 | .13 | .11 | .11 | .12 | .12 | .11 |
| .005 | .14 | .18 | .15 | .15 | .13 | .12 | .18 | .16 | |
| .0025 | .15 | .21 | | | .14 | .14 | | | |

B.P.B. = bromphenolblue, B.C.G. = bromcresolgreen, B. C. P. = bromcresolpurple, C.P.R. = chlorphenolred, B.T.B. = bromthymolblue, P.R. = phenolred, Phpt. = phenolphthalein, T.B. = thymolblue, Thpt. = thymolphthalein.

If the buffer mixture used has an ionic strength larger than .1, a small correction has to be subtracted from the experimental data found in order to relate it to an ionic strength of .1. In Table XI we give the salt correction of the different phthaleins at small ionic strengths of the solution.

For practical purposes we may take the average of all these values in order to find the salt correction of the different phthaleins at low electrolyte content, relating the measurements to an ionic strength of the buffer mixture of .1. The figures found do not agree with the theoretical values calculated on the basis of the equation of Debye and Hückel, the experimental data being smaller. In Table XII we give the calculated values by accepting an average ionic size in the buffer mixtures of 8×10^{-8} (citrate buffers) and 4×10^{-8} (phosphate and carbonate buffers) respectively.

TABLE XII

| Ionic strength solution | Average salt correction phthaleins | Correction calculated | |
|----------------------------|---------------------------------------|------------------------|------------------------|
| | | $a = 8 \times 10^{-8}$ | $a = 4 \times 10^{-8}$ |
| .02 | + .11 | .13 | .15 |
| .01 | + .13 | .16 | .21 |
| .005 | + .15 | .18 | .23 |
| .0025 | + .16 | .20 | .27 |

It may be stated that the salt corrections of bromphenolblue, bromcresol-green, bromcresolpurple and chlorphenolred measured in the citrate buffer mixtures are in close agreement with the theoretical data.

In solutions with a much higher ionic strength than that of the buffer mixture, the difference in the salt correction between the individual indicators is much larger than at low electrolyte content. The kind and the size of the cations and anions present have a large influence; the salt corrections calculated on the basis of the equation of Debye and Hückel as a rule are much larger than the experimental data. Only in the case of bromcresol-purple is there a close agreement between the theoretical and determined values.

In Table XIII we give a summary of the salt corrections found in very dilute buffer mixtures in the presence of .5 N potassium, and sodium chloride respectively. The data have been recalculated for an ionic strength of the buffer mixtures used for comparison of .1.

TABLE XIII

Salt corrections of phthaleins in .5 N KCl and .5 N NaCl as compared with buffer mixtures with an ionic strength of .1

| | B.P.B. | B.C.G. | C.P.R. | B.C.P. | B.T.B. | P.R. | T.B. | Phpt. | Thpt. |
|-----------|--------|--------|--------|--------|--------|------|------|-------|-------|
| .5 N KCl | -.10 | -.12 | -.16 | -.26 | -.20 | -.20 | | | -.19 |
| .5 N NaCl | -.18 | -.16 | -.19 | -.34 | -.28 | -.29 | -.19 | -.21 | |

Bromides, iodides and nitrates have approximately the same influence as chlorides.

In citrate solutions with an ionic strength of .5 the salt error of the phthaleins is much smaller than in .5 N potassium or sodium chloride. This could be expected, as the ionic size of the citrate ions is much larger than that of the chloride ions. So far, however, we are unable to account quantitatively for this difference on the basis of the equation of Debye and Hückel. Other factors such as are mentioned in the first section of this paper seem to play a part.

Summary

1. An attempt has been made to calculate the salt correction of indicators on the basis of the equation of Debye and Hückel. If the ionic strength of the solution is much larger than that in the ordinary buffers, the calculated corrections are higher than the experimental values. Moreover indicators of the same type behave differently.

2. The average salt correction of the different phthaleins at an ionic strength between .1 and .0025 has been given. The values are related to an ionic strength of the buffer solution of .1.

3. In reporting on the salt error of indicators the ionic strength and the composition of the buffer mixtures used for comparison should be mentioned. The salt correction is also dependent upon the properties of the buffer solution.

4. Methylorange and methylred show very small salt errors under different conditions, and therefore are very suitable indicators. Their behavior is explained by the fact that they have a hybrid character. Quite generally it may be expected that indicators which have hybrid properties will be ideal for the measurement of pH.

*Minneapolis,
May, 1928.*

THE VARIATION OF THE EXTINCTION-COEFFICIENT WITH TEMPERATURE

BY B. K. MUKERJI, A. K. BHATTACHARJI AND N. R. DHAR

It has been observed in these laboratories that in several photochemical reactions, even when all other conditions are precisely the same, the photochemical yield per quantum changes markedly with change in the temperature at which the reactions are investigated. Kuhn¹ has shown that, in the photochemical decomposition of gaseous ammonia, the ratio of quanta required to molecules decomposing changes appreciably with temperature. In a recent communication Eggert and co-workers² have shown that in the conversion of ethyl-maleate into the corresponding fumarate by illumination and in the bromination of ethyl maleate to ethyl dibromo-succinate the quantum efficiency varies with the temperature.

It is difficult to offer an explanation for this striking phenomenon, namely, the variation of the quantum yield with temperature, unless it be assumed that the quantity of the light energy of a particular type absorbed by the system also changes with temperature. We are not aware of any investigation on record proving that the amount of light absorption changes with temperature. The object of this paper is to show that the extinction-coefficients of some coloured solutions for the absorption of light in the visible region do vary appreciably with changes in the temperature.

Experimental

For the measurement of the extinction-coefficients a Hilger-Nutting spectrophotometer was used. To isolate any particular region of the spectrum for ease of comparison a shuttered eyepiece was employed. The source of light was a 100 c.p. Point-o-lite lamp working at 220 volts. Two, similar, neutral-tint glass cells with optically-plane parallel ends were used—one for the solution whose extinction-coefficient had to be observed and the other for an equal volume of distilled water so that comparisons might be made precisely under identical conditions of original light intensity.

Preliminary observations showed that both the pencils of light did not in any way lose in intensity by passing through the two empty cells and both the spectra observed were equally bright. The desired temperatures were obtained by placing the solutions in a thermostat maintained constant with a variation of 0.1°. The distilled water to be used was also allowed to attain the same temperature.

The time taken in actually reading the scale after the comparison of the two spectra did not exceed 45 seconds and precautions were taken to ensure constancy of temperature during this interval.

¹ Compt. rend., 177, 956 (1923); 178, 708 (1924).

² Z. Physik, 26, 865 (1925).

In the cases of reacting mixtures, titrations were carefully made to test that no appreciable change takes place at the lower and the higher temperatures during the very short time taken to read the scale on the photometer.

The following experimental results were obtained:

1. Chromic acid—N/40.

Zero error = 0.39.

Thickness of the observation cell = 0.385 cm.

Spectral region: $\lambda = 5160 \text{ \AA}$.

| Temperature | Reading on the density scale | Corrected reading on the density scale | Extinction coefficient |
|-------------|------------------------------|----------------------------------------|------------------------|
| 30°C. | 0.8 | 0.41 | 1.06 |
| 40° | 0.84 | 0.45 | 1.17 |
| 50° | 0.90 | 0.51 | 1.32 |
| 60° | 0.99 | 0.60 | 1.56 |
| 20° | 0.75 | 0.36 | 0.93 |

2. Iodine dissolved in potassium iodide. $I_2 - N/39.6$.

Zero error = 0.40.

Thickness of the observation cell = 0.385 cm.

Spectral region: $\lambda = 5160 \text{ \AA}$.

| Temperature | Reading on the density scale | Corrected reading on the density scale | Extinction coefficient |
|-------------|------------------------------|----------------------------------------|------------------------|
| 10°C. | 1.4 | 1.0 | 2.6 |
| 20° | 1.5 | 1.1 | 2.85 |
| 30° | 1.6 | 1.2 | 3.1 |
| 40° | 1.7 | 1.3 | 3.38 |
| 50° | 1.8 | 1.4 | 3.6 |

3. Iodine dissolved in alcohol. $I_2 - N/39.6$.

Zero error = 0.40.

Thickness of the observation cell = 0.385 cm.

Spectral region: $\lambda = 5160 \text{ \AA}$.

| Temperature | Reading on the density scale | Corrected reading on the density scale | Extinction coefficient |
|-------------|------------------------------|----------------------------------------|------------------------|
| 15°C. | 1.28 | 0.88 | 2.28 |
| 20° | 1.30 | 0.90 | 2.34 |
| 25° | 1.36 | 0.96 | 2.50 |
| 30° | 1.40 | 1.00 | 2.60 |
| 35° | 1.45 | 1.05 | 2.70 |

4. Potassium oxalate and iodine.

 $K_2C_2O_4 - N/29.5; I_2 - N/39.6; KI - N/10.8.$

Zero error = 0.40.

Thickness of the observation cell = 0.385 cm.

Spectral region: $\lambda = 5216 \text{ \AA}.$

| Temperature | Reading on the density scale | Corrected reading on the density scale | Extinction coefficient |
|-------------|------------------------------|----------------------------------------|------------------------|
| 10°C. | 1.01 | 0.61 | 1.60 |
| 15° | 1.12 | 0.72 | 1.87 |
| 20° | 1.21 | 0.81 | 2.10 |
| 25° | 1.26 | 0.86 | 2.23 |
| 30° | 1.34 | 0.94 | 2.44 |

5. Chromic acid and oxalic acid.

 $H_2Cr_2O_7 - N/20; (COOH)_2 - N/28.4.$

Zero error = 0.6.

Thickness of the observation cell = 0.385 cm.

Spectral region $\lambda = N/28.4 \text{ } 4880 \text{ \AA}.$

| Temperature | Reading the density scale | Corrected reading on the density scale | Extinction coefficient |
|-------------|---------------------------|----------------------------------------|------------------------|
| 10°C. | 1.16 | 0.56 | 1.45 |
| 15° | 1.20 | 0.60 | 1.56 |
| 20° | 1.26 | 0.66 | 1.71 |
| 25° | 1.30 | 0.70 | 1.82 |
| 30° | 1.35 | 0.75 | 1.94 |

6. Chromic acid and quinine sulphate in excess of sulphuric acid.

 $\text{Chromic acid} - N/20; \text{Quinine Sulphate} - M/47.$

Zero error = 0.4.

Thickness of the observation cell = 0.385 cm.

Spectral region: $\lambda = 5010 \text{ \AA}.$

| Temperature | Reading on the density scale | Corrected reading on the density scale | Extinction coefficient |
|-------------|------------------------------|----------------------------------------|------------------------|
| 10°C. | 0.88 | 0.48 | 1.25 |
| 15° | 0.99 | 0.59 | 1.53 |
| 20° | 1.10 | 0.70 | 1.82 |
| 25° | 1.18 | 0.78 | 2.02 |
| 30° | 1.22 | 0.82 | 2.13 |

7. Rochelle salt and bromine in presence of sodium acetate.

Rochelle salt — $N/3.03$; Bromine — $N/125$;

Sodium acetate — $N/1.65$.

Zero error = 0.4.

Thickness of the observation cell = 0.385 cm.

Spectral region: $\lambda = 5200 \text{ \AA}$.

| Temperature | Reading on the density scale | Corrected reading on the density scale | Extinction coefficient |
|-------------|------------------------------|----------------------------------------|------------------------|
| 10°C. | 0.82 | 0.42 | 1.09 |
| 15° | 0.91 | 0.51 | 1.32 |
| 20° | 0.95 | 0.55 | 1.43 |
| 25° | 1.00 | 0.60 | 1.55 |
| 30° | 1.07 | 0.67 | 1.74 |

8. Potassium permanganate: KMnO_4 — $N/105.325$.

Zero error = 0.4.

Thickness of the observation cell = 0.385 cm.

Spectral region: $\lambda = 5640 \text{ \AA}$.

| Temperature | Reading the density scale | Corrected reading on the density scale | Extinction coefficient |
|-------------|---------------------------|----------------------------------------|------------------------|
| 10°C. | 0.86 | 0.46 | 1.20 |
| 25° | 0.95 | 0.55 | 1.43 |
| 35° | 1.01 | 0.61 | 1.58 |
| 50° | 1.10 | 0.70 | 1.82 |

9. Sodium nitrite and iodine in presence of sodium acetate.

CH_3COONa — $N/2$; NaNO_2 — $N/1.69$; I_2 — $N/36$.

Zero error = nil.

Thickness of the observation cell = 0.385 cm.

Spectral region: $\lambda = 5280 \text{ \AA}$.

| Temperature | Reading on the density scale | Corrected reading on the density scale | Extinction coefficient |
|-------------|------------------------------|----------------------------------------|------------------------|
| 10°C. | 0.29 | 0.29 | 0.75 |
| 20° | 0.30 | 0.30 | 0.78 |
| 30° | 0.32 | 0.32 | 0.83 |
| 40° | 0.34 | 0.34 | 0.88 |

10. Sodium formate and iodine in presence of sodium acetate.

$\text{HCOONa} - \text{N}/2.14; \text{I}_2 - \text{N}/39.64; \text{CH}_3\text{COONa} - \text{N}/$

Zero error = nil.

Thickness of the observation cell = 0.385 cm.

Spectral region: $\lambda = 5280 \text{ \AA}$.

| Temperature | Reading on the density scale | Corrected reading on the density scale | Extinction coefficient |
|-------------|------------------------------|----------------------------------------|------------------------|
| 10°C. | 0.43 | 0.43 | 1.10 |
| 20° | 0.48 | 0.48 | 1.24 |
| 30° | 0.53 | 0.53 | 1.36 |
| 40° | 0.56 | 0.56 | 1.45 |

11. Ferrous sulphate and iodine.

$\text{FeSO}_4 - \text{N}/4; \text{I}_2 - \text{N}/39.64.$

Zero error = nil.

Thickness of the observation cell = 0.385 cm.

Spectral region: $\lambda = 5280 \text{ \AA}$.

| Temperature | Reading on the density scale | Corrected reading on the density scale | Extinction coefficient |
|-------------|------------------------------|----------------------------------------|------------------------|
| 10°C. | 0.47 | 0.47 | 1.22 |
| 20° | 0.48 | 0.48 | 1.25 |
| 30° | 0.49 | 0.49 | 1.27 |
| 40° | 0.50 | 0.50 | 1.30 |

12. Eosin.

Zero error = nil.

Thickness of the observation cell = 0.385 cm.

Spectral region: $\lambda = 5650 \text{ \AA}$.

| Temperature | Reading on the density scale | Corrected reading on the density scale | Extinction coefficient |
|-------------|------------------------------|----------------------------------------|------------------------|
| 10°C. | 0.12 | 0.12 | 0.31 |
| 20° | 0.18 | 0.18 | 0.46 |
| 30° | 0.225 | 0.225 | 0.58 |
| 40° | 0.28 | 0.28 | 0.73 |

13. Ammonium oxalate and iodine.

$(\text{NH}_4)_2\text{C}_2\text{O}_4 - \text{N}/3.02; \text{I}_2 - \text{N}/40.$

Zero error — nil.

Thickness of the observation cell = 0.385 cm.

Spectral region: $\lambda = 5650 \text{ \AA}.$

| Temperature | Reading on the density scale | Corrected reading on the density scale | Extinction coefficient |
|-------------|------------------------------|----------------------------------------|------------------------|
| 10°C. | 0.30 | 0.30 | 0.78 |
| 20° | 0.36 | 0.36 | 0.935 |
| 30° | 0.42 | 0.42 | 1.09 |
| 40° | 0.48 | 0.48 | 1.25 |

14. Copper sulphate.

$\text{CuSO}_4, 5\text{H}_2\text{O} - \text{N}.$

Zero error = nil.

Thickness of the observation cell = 0.385 cm.

Spectral region $\lambda = 6300 \text{ \AA}.$

| Temperature | Reading on the density scale | Corrected reading on the density scale | Extinction coefficient |
|-------------|------------------------------|----------------------------------------|------------------------|
| 10°C. | 0.31 | 0.31 | 0.805 |
| 20° | 0.35 | 0.35 | 0.909 |
| 30° | 0.40 | 0.40 | 1.04 |
| 40° | 0.45 | 0.45 | 1.14 |

15. Cuprous chloride (HCl).

Zero error = 0.2.

Thickness of the observation cell = 0.385 cm.

Spectral region $\lambda = 6000 \text{ \AA}.$

| Temperature | Reading on the density scale | Corrected reading on the density scale | Extinction coefficient |
|-------------|------------------------------|----------------------------------------|------------------------|
| 15°C. | 0.58 | 0.38 | 0.98 |
| 20° | 0.6 | 0.40 | 1.04 |
| 30° | 0.66 | 0.46 | 1.20 |
| 40° | 0.70 | 0.50 | 1.30 |

Discussion

In all the cases investigated by us we find that the extinction-coefficient increases with the increase in temperature of the solutions. In some cases the extinction-coefficient increases three-fold for a 30° rise of temperature of the solutions. This shows that the amount of absorption of light increases considerably with increase of temperature.

We can explain these results from the point of view of the change of hydration of the solutes at higher temperatures. We can generally diminish the complexity of the solvates by raising the temperature and this frequently leads to changes in the absorption. As the solvates become simpler the absorption bands become broader. That is, the absorption of light may increase by increasing the temperature. It is generally found that the effect of increasing the temperature of the solution is the same as that of increasing the concentration of the solute. In both cases there is a widening of the absorption bands—that is, the absorption of light increases owing to the solvates becoming simpler.¹

In all the cases investigated straight lines are obtained when the extinction-coefficients are plotted against the temperatures. The diagrams are therefore not given.

This increase in the extinction-coefficient with temperature will at any rate explain the frequent increase in the quantum yield with temperature.

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June, 1927.*

¹ Compare H. C. Jones: "The Nature of Solutions," p. 331.

PROPERTIES OF SUBSTANCES AND MIXTURES AT THE
ABSOLUTE ZERO OF TEMPERATURE CONNECTED
WITH CHANGE OF STATE

BY R. D. KLEEMAN

1. Extensions of Some of the Results obtained previously

The writer in a previous paper showed¹ that the controllable internal energy u and the controllable entropy S are each zero for a substance or mixture in the condensed state under its vapor pressure at the absolute zero of temperature, a point called the absolute zero of control, or

$$S = 0 \quad (1)$$

$$u = 0 \quad (2)$$

under these conditions. It was also shown² that the entropy is also zero for all other states at the absolute zero of temperature. If we make use of the postulates that $\left(\frac{\partial S}{\partial T}\right)_v$ and $\left(\frac{\partial S}{\partial v}\right)_T$ are not discontinuous for a homogeneous mass of matter of volume v and absolute temperature T , already used in the first paper quoted, it will follow from the Calculus that

$$\left(\frac{\partial S}{\partial T}\right)_v = 0 \quad (3)$$

$$\left(\frac{\partial S}{\partial v}\right)_T = 0 \quad (4)$$

for all states of matter at the absolute zero of temperature. From these equations it can then be deduced similarly as in the papers quoted for the case that the substance is under its vapor pressure, that

$$\left(\frac{\partial u}{\partial T}\right)_v = c_v = c_{v\infty} = 0 \quad (5)$$

$$\left(\frac{\partial^2 u}{\partial T^2}\right)_v = \left(\frac{\partial c_v}{\partial T}\right)_v = \left(\frac{\partial v_{v\infty}}{\partial T}\right)_v = 0 \quad (6)$$

$$\left(\frac{\partial p}{\partial T}\right)_v = 0 \quad (7)$$

$$\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0 \quad (8)$$

$$\left(\frac{\partial v}{\partial T}\right)_p = 0 \quad (9)$$

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p = 0 \quad (10)$$

$$c_p = c_{p\infty} = 0 \quad (11)$$

$$\left(\frac{\partial c_p}{\partial T}\right)_p = \left(\frac{\partial c_{p\infty}}{\partial T}\right)_p = 0 \quad (12)$$

¹ J. Phys. Chem., 31, 747 (1927).

² J. Phys. Chem., 31, 940 (1927).

for all states of matter at $T = 0$, where c_v and c_p denote the specific heat of the condensed substance at constant volume v and pressure p respectively, and c_{v_0} and c_{p_0} the corresponding specific heats of the vapor.¹

2. Properties of the Heat and External Work of Evaporation at the Absolute Zero of Temperature

2. If L denote the internal heat of evaporation of a substance or mixture and w the external work done during evaporation

$$\frac{L + w}{T} = 0 \quad (13)$$

at the absolute zero of temperature, since according to the previous Section no change in entropy takes place. Since

$$w = p(v_\infty - v_0) = RT \quad (14)$$

according to the gas equation, where v_∞ denotes the volume of the substance in the gaseous state at the absolute zero of temperature, we have

$$w = 0 \quad (15)$$

under these conditions. It follows then that

$$L = 0 \quad (16)$$

or no change in internal energy takes place during evaporation.

Another proof of this remarkable result may be based on Clapeyron's equation

$$L = \left\{ T \frac{dp}{dT} - p \right\} (v_2 - v_1) \quad (17)$$

where v_2 and v_1 denote the volumes of the vapor and the condensed phase respectively. This equation may be written

$$p(v_2 - v_1) = \frac{p}{T \frac{dp}{dT} - p} L \quad (18)$$

The factor of L is indeterminate in form at the absolute zero of temperature, since $T = 0$ and $p = 0$. Its value can easily be found and shown to be finite by successive differentiations. Therefore since $p(v_2 - v_1) = 0$ we have $L = 0$.

This result may be explained by supposing that during the separation of the molecules during evaporation attraction is the outstanding force over a certain range of distances and repulsion the outstanding force over the remaining range, and that the work done by the forces of repulsion is equal to the work done against the forces of attraction. This is rendered probable by

¹ Equations (9) and (10) may be obtained from equations (7) and (8) and the equations $\left\{ \left(\frac{\partial p}{\partial T} \right)_v = - \left(\frac{\partial p}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p, \left(\frac{\partial^2 p}{\partial T^2} \right)_v = \frac{\partial^2 p}{\partial v \partial T} \left(\frac{\partial v}{\partial T} \right)_p - \left(\frac{\partial p}{\partial v} \right)_T \left\{ \frac{\partial}{\partial p} \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_v - \left(\frac{\partial^2 v}{\partial T^2} \right)_p \right\}$ obtained by means of the Calculus.

considering the continuous variation of p according to an equation of state like van der Waals'. If the initial and final pressure is zero during evaporation and the process is supposed to be continuous, the pressure will at first be positive, pass through zero, become negative, and pass again through zero. The positive and negative pressures correspond to repulsion and attraction being respectively the outstanding forces between the molecules.

The result may also be explained by supposing that the molecular and atomic forces of attraction are considerably diminished if not altogether deleted on reducing the temperature to the absolute zero. Evidence that this may be the case will appear from Section 7.

Thirdly it may be explained by supposing that the work done against the atomic and molecular forces during evaporation is counterbalanced by the evolution of an equal amount of heat drawn from the intra-atomic energy. If this or the foregoing is the true explanation, the electronic configuration of the atoms in the gaseous state at the absolute zero of temperature is considerably different from that in the condensed state, and different from that in the gaseous state at higher temperatures. This is rendered highly likely by the marked changes that are predicted in Section 8 to take place in the value of the specific heat of a gas near the absolute zero of temperature. These changes are specially striking in the case of a monatomic gas since they can only be caused by changes in the electronic configurations of the atoms.

It might be argued that w or the product $p(v_2 - v_1)$ in equation (18) may not be zero at the absolute zero of temperature. Now the factor of L in the equation is positive as can easily be shown (thus on differentiating numerator and denominator thrice with respect to T it becomes equal to $\frac{1}{2}$), and hence L and $p(v_2 - v_1)$ if finite have the same sign. But they must have different signs according to equation (13), hence we conclude that

$$w = p(v_2 - v_1) = p(v_\infty - v_0) = 0 \quad (19)$$

at the absolute zero of temperature.

Expressions for the differential coefficients of L in terms of the differential coefficients of the specific heats may be obtained on writing

$$L = u_\infty - u_0 \quad (20)$$

where u_∞ and u_0 denote the internal energies in the vaporous and condensed states respectively. On differentiating this equation n times with respect to T it becomes

$$\frac{d^n L}{dT^n} = \frac{d^n u_\infty}{dT^n} - \frac{d^n u_0}{dT^n} = \frac{d^{n-1}}{dT^{n-1}} \{c_{i_\infty} - c_{i_0}\} \quad (21)$$

where c_{i_∞} and c_{i_0} denote the internal specific heats of the vaporous and condensed states respectively. The first and second coefficient assume special values. We have

$$\frac{dL}{dT} = \frac{du_\infty}{dT} - \frac{du_0}{dT} = 0 \quad (22)$$

and

$$\frac{d^2 L}{dT^2} = \frac{d^2 u_\infty}{dT^2} - \frac{d^2 u_0}{dT^2} = 0 \quad (23)$$

according to equations (51) and (56) given in a previous paper¹ and extended by equations (5), (6), (7), (8), (9) and (10).

Clapeyron's equation may be written

$$\frac{L}{w} = \frac{T}{p} \frac{dp}{dT} - 1$$

The right hand side is evidently not zero but finite when $T = 0$, taking into account equations (36) and (37) given in the paper just quoted. On obtaining the limiting value of the left hand side by means of equations (23), (22), (16), and (15) it appears that

$$\frac{dw}{dT} = 0 \quad (24)$$

and

$$\frac{d^2w}{dT^2} = 0 \quad (25)$$

when $T = 0$.

Equation (13) may be written

$$\frac{L_t}{T} = 0 \quad (26)$$

where L_t denotes the total heat of evaporation, and hence we have directly

$$L_t = 0 \quad (27)$$

and

$$\frac{dL_t}{dT} = 0 \quad (28)$$

at the absolute zero of temperature, which corroborates equations (15), (16), (22) and (24).

3. Properties of the Condensed State at the Absolute Zero of Temperature

If a substance is passed from the state 1 to the state 2 under any given pressures at the absolute zero of temperature, we have

$$\frac{L + w}{T} = 0$$

as before, where L denotes the increase in internal energy and w the external work done. Therefore, since $T = 0$

$$L = -w \quad (29)$$

or the increase in internal energy of a substance is equal to the external work done upon it.

If the two states are stable under their vapor pressures, which would be zero, $w = 0$ and hence $L = 0$ as obtained before.

¹ J. Phys. Chem., 31, 937 (1927).

If we write

$$L = u_2 - u_1 \quad (30)$$

where u_2 and u_1 are the internal energies of the two states, one or both of which correspond to the application of an external pressure, it can be deduced that in general

$$\left(\frac{\partial^n L}{\partial T^n}\right)_p = \left[\frac{\partial^{n-1}}{\partial T^{n-1}} \{c_{p2} - c_{p1}\}\right]_p \quad (31)$$

$$\left(\frac{\partial^n L}{\partial T^n}\right)_v = \left[\frac{\partial^{n-1}}{\partial T^{n-1}} \{c_{v2} - c_{v1}\}\right]_v \quad (32)$$

4. The Form of the Equation of State of the Vapor of a Substance at or near the Absolute Zero of Temperature

Let us write

$$w = p(v_2 - v_1) = N\beta RT \quad (33)$$

for the work of evaporation of a substance, where N denotes the total number of molecules it contains and β a function of T whose nature we will proceed to investigate. On differentiating the equation totally with respect to T we obtain

$$\frac{dw}{dT} = NRT \frac{d\beta}{dT} + \beta NR + \beta RT \frac{dN}{dT}$$

Hence

$$\beta = 0 \quad (34)$$

at the absolute zero of temperature according to equation (24) and since $T = 0$. On differentiating again we obtain

$$\frac{d^2w}{dT^2} = NRT \frac{d^2\beta}{dT^2} + 2NR \frac{d\beta}{dT} + 2T \frac{Rd\beta}{dT} \frac{dN}{dT} + 2\beta \frac{RdN}{dT} + \beta T \frac{Rd^2N}{dT^2}$$

which gives

$$\frac{d\beta}{dT} = 0 \quad (35)$$

according to equations (34) and (25) and since $T = 0$. The differentiation may also be carried out at constant volume or constant pressure since β is a function of the temperature only.

β must evidently become approximately equal to unity, for values of T not far removed from the absolute zero. This condition and equations (35) and (34) are evidently satisfied if we write

$$\beta = 1 - a^{-T}$$

where a is a constant greater than unity. The equation of state of the vapor of a substance close to $T = 0$ may accordingly (provisionally) be written

$$pv = NRT(1 - a^{-T}) \quad (36)$$

According to the kinetic theory of gases we may write

$$pv = KNV^2 = N\beta RT$$

and hence

$$KV^2 = \beta RT \quad (37)$$

where V denotes the mean square molecular velocity and K is a constant. This equation indicates that the kinetic energy of a gas is not proportional to the temperature near the absolute zero. At the absolute zero since $\beta = 0$ and $T = 0$, it is interesting to notice, the equation gives

$$V = 0 \quad (38)$$

On differentiating equation (37) twice totally with respect to T we obtain

$$2K \left\{ \left(\frac{dV}{dT} \right)^2 + V \frac{d^2V}{dT^2} \right\} = RT \frac{d^2\beta}{dT^2} + 2R \frac{d\beta}{dT}$$

At the absolute zero of temperature this equation becomes

$$\frac{dV}{dT} = 0 \quad (39)$$

according to equation (35) and since $T = 0$ and $V = 0$. This equation also holds at constant volume or constant pressure. The change in molecular motion of a gas with increase in temperature at the absolute zero is thus zero, suggesting the existence of a special molecular inertness at that point.

The bearing of this result on the specific heat will appear if we consider a monatomic gas whose energy we will suppose consists of kinetic energy of motion of translation only. We will then have

$$c_{v\infty} = \frac{d}{dT} (KNV^2) = KN_2 V \frac{dV}{dT} \quad (40)$$

Thus $c_{v\infty}$ is zero at the absolute zero of temperature if we assume, as is usually done, that the velocity of molecular motion of translation is zero, and take equation (39) into account. It is however more logical to deduce thermodynamically that V is zero (equation (38)).

On differentiating the equation with respect to T we have

$$\frac{dc_{v\infty}}{dT} = KN_2 \left(\frac{dV}{dT} \right)^2 + KN_2 V \frac{d^2V}{dT^2}$$

The right hand side is zero according to equations (38) and (39), and therefore

$$\frac{dc_{v\infty}}{dT} = 0 \quad (41)$$

Thus it appears that the properties of the specific heat of a gas expressed by equations (5) and (6) are in the case of a monatomic gas intimately connected with equations (38) and (39) referring to the velocity of molecular motion.

In the case of a complex gas we may write

$$c_{v\infty} = \frac{dT}{dT} (KNV^2) + \frac{du_{\infty}}{dT} \quad (42)$$

where u_{∞} denotes the internal energy of the gas other than kinetic energy of motion of translation. The first term on the right hand side of the equation is zero at $T = 0$, as we have just seen, and hence

$$\frac{du_{\infty}}{dT} = 0 \quad (43)$$

by the help of equation (5). On differentiating the preceding equation with respect to T it can be shown on referring to equations (38), (39) and (6) that

$$\frac{d^2u_{\infty}}{dT^2} = 0 \quad (44)$$

Equations (44) and (43) also hold if the differentiations are carried out at constant volume or constant pressure since this holds for equation (39).

It is of interest to note that if we write

$$KNV^2 = RT$$

according to the old form of the gas equation, and differentiate this equation with respect to T we obtain

$$KN_2V \frac{dV}{dT} = R \quad (45)$$

Since an infinite value of dv/dt is physically absurd, at $T = 0$ this becomes

$$0 = R$$

if we assume that $V = 0$. But this is inadmissible. Hence R should have a factor in the gas equation besides T which is a function of T . This factor β we have already shown should exist from entirely different considerations.

The gas degeneration shown by the gas equation has been suspected from the slight decrease of the specific heat at constant volume of helium as the temperature is lowered, obtained by Eucken.¹ It has been considered mathematically by Sackur,² Tetrode,³ Keesom,⁴ Lenz and Sommerfeld,⁵ Scherrer,⁶ Planck⁷ and Nernst,⁸ usually from the point of view of quantizing the specific heat.⁹

¹ Sitzungsber. preuss. Akad. Wiss., 144 (1912).

² Ann. Physik, (4), 40, 67 (1913).

³ Physik. Z., 14, 212 (1913).

⁴ Physik. Z., 15, 695 (1914).

⁵ "Vorträge über die kinetische Theorie der Materie und der Elektrizität". Wolfskehl Kongress in Göttingen, p. 125, (1914).

⁶ Göttinger Nachrichten, 8, July (1916).

⁷ Ann. Physik., (4), 50, 385 (1916).

⁸ "Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes", p. 154, (1918).

⁹ A purely thermodynamical treatment for temperatures not very far removed from the absolute zero has been given by the writer. J. Franklin Inst., 206, 691 (1928).

5. The Temperature Coefficient of the Pressure of the Saturated Vapor of a Substance or Mixture at $T = 0$.

Let us write equation (33) in the form

$$v_2 = \frac{\beta RT}{p} \quad (46)$$

The right hand side when $T = 0$ is indeterminate, and its limiting value is therefore

$$v_2 = \frac{\beta R + RT \frac{d\beta}{dT}}{\frac{dp}{dT}}$$

According to equations (34), (35) and equation (36) given in a previous paper¹, it is still indeterminate and therefore

$$v_2 = \frac{2R \frac{d\beta}{dT} + RT \frac{d^2\beta}{dT^2}}{\frac{d^2p}{dT^2}}$$

which is still indeterminate according to equation (35), equation (37) given in the paper just quoted, and since $T = 0$, and therefore

$$v_2 = \frac{3R \frac{d^2\beta}{dT^2} + RT \frac{d^3\beta}{dT^3}}{\frac{d^3p}{dT^3}}$$

Since $v_2 = \infty$ when $T = 0$ it follows from this equation that

$$\frac{d^3p}{dT^3} = 0 \quad (47)$$

This equation refers to the pressure of the saturated vapor of a condensed substance. But it should be noted that it does not follow therefore that

$$\left(\frac{d^3p}{dT^3}\right)_v = 0$$

for the condensed substance. On the other hand if this equation could be proved, equation (47) could immediately be deduced from it along the line of reasoning given in a previous paper.¹

6. Properties of the Heat and Work of Mixing of Substances in the Gaseous State at the Absolute Zero of Temperature

Let us pass a number of condensed substances through the following isothermal cycle at the absolute zero of temperature:—

a) Mix the substances under pressures equal to their vapor pressures, giving rise to an increase in internal energy equal to h_m .

¹ J. Phys. Chem., 31, 937 (1927).

b) Evaporate the mixture, with attendant increase in internal energy equal to L .

c) Separate the constituents of the resultant gas from each other. The internal energy is increased by $-h_{m\infty}$.

d) Condense the constituents separately, giving rise to an increase in internal energy equal to $-\Sigma L_a$.

Since the total change in internal energy is zero

$$L - \Sigma L_a = \Delta L = h_{m\infty} - h_m \quad (48)$$

Now $\Delta L = 0$ and $h_m = 0$ according to equation (16) and equation (30) given in a previous paper,¹ and hence

$$h_{m\infty} = 0 \quad (49)$$

On differentiating equation (48) twice in succession totally with respect to T it can easily be shown by means of equations (22), (23), and equations (47) and (46) given in a previous paper¹ that

$$\frac{dh_{m\infty}}{dT} = 0 \text{ and } \frac{d^2h_{m\infty}}{dT^2} = 0 \quad (50)$$

We have directly that

$$\Delta \left(\frac{\partial u_{\infty}}{\partial T} \right)_v = \left(\frac{\partial h_{m\infty}}{\partial T} \right)_v = 0 \quad (51)$$

and

$$\Delta \left(\frac{\partial^2 u_{\infty}}{\partial T^2} \right)_v = \left(\frac{\partial^2 h_{m\infty}}{\partial T^2} \right)_v = 0 \quad (52)$$

by means of equations (5) and (6).

Equation (49) may be written

$$h_{m\infty} = h_f \cdot \Delta N = 0 \quad (53)$$

where ΔN denotes the change in the number of molecules on mixing the gases, and h_f the heat absorbed corresponding to each molecule changed. Thus either h_f or ΔN must be zero. It can easily be shown by means of equation (50) that if h_f is zero this also holds for the first and second differential coefficients with respect to T , and if ΔN is zero this also holds for its first and second differential coefficients.

The external work A_{∞} done during the process of mixing is given by

$$H_{m\infty} = h_{m\infty} + A_{\infty}$$

where $H_{m\infty}$ denotes the heat absorbed during the process of mixing. Besides we have the well known equation

$$H_{m\infty} = T \left(\frac{\partial p}{\partial T} \right)_v$$

¹ R. D. Kleeman: J. Phys. Chem., 31, 1559 (1927).

By means of these two equations and equations (8), (7), (49), (51), (52), and the equation $T = 0$ it can easily be shown that

$$H_{m\infty} = 0 \text{ and } A_{\infty} = 0 \quad (54)$$

$$\left(\frac{\partial H_{m\infty}}{\partial T}\right)_v = 0 \text{ and } \left(\frac{\partial^2 H_{m\infty}}{\partial T^2}\right)_v = 0 \quad (55)$$

$$\left(\frac{\partial A_{m\infty}}{\partial T}\right)_v = 0 \text{ and } \left(\frac{\partial^2 A_{m\infty}}{\partial T^2}\right)_v = 0 \quad (56)$$

7. Properties of the Change in Free Energy and the Heat of Formation of Substances in the Gaseous State at the Absolute Zero of Temperature

The change in free energy ΔF is given by

$$\Delta F = \Delta u - T\Delta S + \Delta pv \quad (57)$$

If this equation is applied to gases at the absolute zero of temperature

$$\Delta u = p_{m\infty} = 0$$

and

$$\Delta pv = \Delta N\beta RT = 0$$

according to equation (49), and thus

$$\Delta F = 0 \quad (58)$$

under these conditions. On differentiating equation (57) thrice with respect to T at constant volume we have

$$\begin{aligned} \left(\frac{\partial \Delta F}{\partial T}\right)_v &= \left(\frac{\partial \Delta u}{\partial T}\right)_v - \Delta S - T \left(\frac{\partial \Delta S}{\partial T}\right)_v + \left(\frac{\partial \Delta N\beta RT}{\partial T}\right)_v, \\ \left(\frac{\partial^2 \Delta F}{\partial T^2}\right)_v &= \left(\frac{\partial^2 \Delta u}{\partial T^2}\right)_v - 2 \left(\frac{\partial \Delta S}{\partial T}\right)_v - T \left(\frac{\partial^2 \Delta S}{\partial T^2}\right)_v + \left(\frac{\partial^2 \Delta N\beta RT}{\partial T^2}\right)_v, \\ \left(\frac{\partial^3 \Delta F}{\partial T^3}\right)_v &= \left(\frac{\partial^3 \Delta u}{\partial T^3}\right)_v - 3 \left(\frac{\partial^2 \Delta S}{\partial T^2}\right)_v - T \left(\frac{\partial^3 \Delta S}{\partial T^3}\right)_v + \left(\frac{\partial^3 \Delta N\beta RT}{\partial T^3}\right)_v. \end{aligned}$$

From these equations we obtain

$$\left(\frac{\partial \Delta F}{\partial T}\right)_v = 0 \quad (59)$$

$$\left(\frac{\partial^2 \Delta F}{\partial T^2}\right)_v = 0 \quad (60)$$

$$\left(\frac{\partial^3 \Delta F}{\partial T^3}\right)_v = -\frac{1}{2} \left(\frac{\partial^3 u}{\partial T^3}\right)_v + 3R \left(\frac{\partial^2 \Delta \beta N}{\partial T^2}\right)_v \quad (61)$$

at the absolute zero of temperature by means of equations (1), (3), (5), (6), (35), (34) and equation (11) given in a previous paper¹.

We have seen that according to equation (53) either ΔN or h_f is zero at $T = 0$. If we are dealing with a finite mass of gas

$$\Delta N = 0 \quad (62)$$

according to a previous paper².

¹ J. Phys. Chem., 31, 1559 (1927).

² R. D. Kleeman: J. Franklin Inst., 206, 691 (1928).

If however the mass of gas considered is infinite ΔN becomes finite, if it is at all possible that α molecule may exist in the gaseous state at $T = 0$, since h_m is zero independent of mass, the remarkable and important result is obtained from equation (53) that

$$h_f = 0 \quad (63)$$

at $T = 0$, or the heat of formation is zero at the absolute zero of temperature.

On differentiating equation (53) with respect to T at constant volume we obtain

$$\left(\frac{\partial \Delta N}{\partial T}\right)_v h_f + \Delta N \left(\frac{\partial h_f}{\partial T}\right)_v = \left(\frac{\partial h_{m\infty}}{\partial T}\right)_v = 0. \quad (64)$$

at $T = 0$ according to equation (51). If as before we deal with an infinite mass of gas we obtain ΔN finite, and since the equation holds independent of the mass of gas we obtain

$$\left(\frac{\partial h_f}{\partial T}\right)_v = 0 \quad (65)$$

by the help of equation (63). On differentiating equation (64) with respect to T at constant volume it may similarly be shown that

$$\left(\frac{\partial^2 h_f}{\partial T^2}\right)_v = 0 \quad (66)$$

by the help of equations (65), (63) and (52).

Equation (63) suggests that the atomic forces are small or disappear altogether at the absolute zero of temperature, which was also suggested by the results of Section 2. The effect of the atomic forces of attraction during combination may of course be balanced by that of repulsion, but this is hardly likely to hold in general.

8. Properties of the Internal Specific heat of a Vapor in Contact with the Condensed State

Let us pass a substance initially in the condensed state through the following cycle:—

a) Allow the substance to evaporate, giving rise to a change in internal energy equal to L .

b) Raise the temperature of the resultant gas by dT , giving rise to an increase in internal energy equal to $c_{i\infty} \cdot dT$, where $c_{i\infty}$ denotes the internal specific heat.

c) Condense the gas, giving rise to an increase in internal energy equal to $-(L + dL)$.

d) Lower the temperature of the condensed substance by dT , giving rise to an increase in internal energy equal to $c_i \cdot dT$, where c_i denotes the internal specific heat of the condensed state.

Since the total change in internal energy is zero we have

$$c_{i\infty} = \frac{dL}{dT} + c_i \quad (67)$$

Since L is zero when $T = 0$, $\frac{dL}{dT}$ is positive up to a value T_m of the temperature given by

$$\frac{dL}{dT} = 0$$

for higher temperatures $\frac{dL}{dT}$ is negative. Thus from the absolute zero of temperature up to the value T_m the internal specific heat of the vapor is greater than that of the condensed state, and in fact is likely to be many times greater as will be shown presently. Corresponding to the temperature T_m

$$c_{i\infty} = c_l \quad (68)$$

and for higher temperatures

$$c_{i\infty} < c_l$$

If a similar cycle is carried out with the substance initially at $T = 0$ and the temperature is then raised by T_m instead of by dT , it can easily be shown that

$$\int_0^{T_m} c_{i\infty} \cdot dT = L_m + \int_0^{T_m} c_l \cdot dT \quad (69)$$

where L_m denotes the internal heat of evaporation at the temperature T_m . On account of the large value L_m is likely to have, it follows from this equation that the average value of $c_{i\infty}$ between 0 and T_m is likely to be many times the average value of c_l .

We saw in Section 2 that the internal heat of evaporation is zero on evaporating a substance at the absolute zero of temperature. Therefore on increasing the temperature of the vapor its potential energy of attraction is greatly increased since the internal heat of evaporation now assumes a large value. The specific heat is increased correspondingly since the increase in potential energy can only take place at the expense of heat energy absorbed from the outside. Since this also holds when the vapor is in the atomic state, an increase in temperature near the absolute zero must be attended by very pronounced changes in the electronic configuration of the atoms, which may be said to return from an abnormal state to the normal state.

9. The Heat of Formation of Molecules in the Gaseous State at Infinite Volume at a Finite Temperature

Let us pass a number of substances in the gaseous state at infinite volume initially at the absolute zero of temperature through the following cycle:—

a) Mix the gases. No change in internal energy takes place according to equation (63).

b) Raise the temperature of the gaseous mixture to T at constant volume. The increase in internal energy is

$$\int_0^T c_{i\infty} \cdot \partial T$$

where c_i denotes the internal specific heat.

c) Separate the gas into its constituents, which gives rise to an increase in internal energy equal to

$$- h_f \cdot \Delta N.$$

d) Lower the temperature of the gases to zero at constant volumes, giving rise to an increase in internal energy equal to

$$- \Sigma \int_0^T c_{i\infty} \cdot \partial T$$

Since the total change in internal energy is zero

$$h_f \cdot \Delta N = - \Delta \int_0^T c_{i\infty} \cdot \partial T \quad (70)$$

when we are dealing with a finite mass $\Delta N = 0$ according to a previous paper¹, but ΔN may be finite when the mass of gas is taken infinite.

The right hand side of the foregoing equation is equal to $-\Delta N$ multiplied by a similar integral involving a gram molecule of the complex substance in a partly dissociated state. And since we may suppose that we are dealing with a number of complex molecules equal to $-\Delta N$ at T which remain undissociated till $T = 0$ is reached, the foregoing equation may be written

$$h_f = - \Delta \int_0^T c'_{i\infty} \cdot \partial T \quad (71)$$

where $\Delta c'_{i\infty}$ represents the difference between the specific heat per mol of the *undissociated* complex substance and the specific heats of its *complete* dissociation products. Hence when h_f has values above the order $\pm 10^3$ cal. per mol the specific heat of the complex molecules has for certain temperatures abnormally large or abnormally small values depending on the sign of h_f .

10. The Temperature of a Substance cannot be Reduced to the Absolute Zero in a Finite Time

Suppose that the temperature of a substance is reduced by passing it through a succession of Carnot's cycles involving a transference of heat from a low to a high temperature. Let the heat absorbed per second per unit

change of volume at the low temperature be $\left(\frac{\partial Q}{\partial v}\right)_T$. The heat absorbed

¹ J. Franklin Inst., 206, 691 (1928).

during the time ∂t is then $T \left(\frac{\partial p}{\partial T} \right)_v \cdot \partial t$ by the help of the thermodynamical equation $\left(\frac{\partial Q}{\partial v} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_v$. This gives rise to a drop ∂T in temperature, and accordingly

$$T \left(\frac{\partial p}{\partial T} \right)_v \cdot \partial t = -c_p \cdot \partial T$$

or

$$\partial t = \frac{c_p}{T \left(\frac{\partial p}{\partial T} \right)_v} \cdot \partial T \quad (72)$$

where c_p denotes the specific heat of the substance. Now according to equations (11), (12), (7) and (8) we may write this equation in the form

$$\partial t = - \frac{a_1 T^3}{T_1 a_2 T^3} \cdot \partial T = - \frac{a_1}{a_2} \frac{\partial T}{T_1}$$

close to the absolute zero of temperature, where a_1 and a_2 are constants. On integrating it between the limits t and \circ , and \circ and T , we obtain

$$t = \frac{a_1}{a_2} \left\{ \ln T - \ln \circ \right\} = \infty,$$

or it takes an infinitely long time to reduce the temperature of the substance from T to \circ in this way.

If the substance radiates like a black body it loses an amount of heat aT^4 per second, and hence

$$aT^4 \cdot \partial t = -c_p \cdot \partial T$$

or

$$\partial t = - \frac{c_p}{aT^4} \cdot \partial T = \frac{a_1}{a} \frac{\partial T}{T} \quad (73)$$

where a is a constant. The integration of this equation gives

$$t = \left[\frac{a_1}{a} \ln T \right]_0^T = \infty$$

or, as before, it takes an infinitely long time for a substance to decrease in temperature from T to \circ by radiation.

Thus it is hardly likely that there is matter in the Universe whose temperature is at the absolute zero unless it began that way. But since radiation of the heavenly bodies into space has been going on for millions of years, the temperature of some of them must be close to the absolute zero. Since some substances may become unstable under these conditions some interesting astronomical possibilities are opened up.

11. The Controllable Entropy is Positive and can be Infinite only when the Temperature is Infinite.

The entropy S of a substance at the finite temperature T and *infinite* volume is given by

$$S = \int_0^T \frac{c_{v\infty}}{T} \cdot \partial T \quad (74)$$

since the adiabatic of zero entropy corresponds to $T = 0$, where $c_{v\infty}$ denotes the specific heat at constant infinite volume. The lower limit of the integral is zero according to equations (5) and (6), and hence S is *positive* and *finite*. The entropy corresponding to a *finite* volume v is given by a similar expression, which, as before is *positive* and *finite* according to equations (5) and (6). The controllable entropy is therefore a positive quantity whose value can be infinite only when the temperature is infinite.

SOLUBILITY RELATIONSHIPS OF LACTOSE-SUCROSE SOLUTIONS

I. Lactose-Sucrose Solubilities at Low Temperatures

BY PHILIP N. PETER*

A study of the solubility relationships of the several forms of lactose in pure solution and of the principles governing the separation of this sugar from such a solution has been made by Hudson.¹ In the presence of certain dissolved substances, however, i.e. sucrose, ammonia, etc., the rate of separation of the solid phase and other physical relationships of these solutions are materially altered. These phenomena are of significance in a consideration of the problem of lactose separation from heterogeneous mixtures, such as ice cream and condensed milk, wherein supersaturated states may exist.

In order to determine the extent of the deviation from the principles which hold for pure solutions a study of certain physical relationships of lactose solutions in the presence of sucrose and of other dissolved substances has been initiated. This first investigation deals with the determination of the solubility relationships of lactose-sucrose solutions at low temperatures.

During the past few years several papers which have a bearing on lactose-sucrose solubilities in aqueous solution have been published. Jackson and Silsbee² present results and discuss the saturation relations in mixtures of sucrose, dextrose and levulose. Jenkins³ has determined the effect of various factors upon the velocity of crystallization of substances from solution, lactose being one of the substances used. Palmer and Dahle⁴ and Lucas and Spitzer⁵ have investigated lactose crystallization in sandy ice cream. Dahle⁶ further discusses the sandy ice cream problem and presents results showing the influence of glucose, gelatin and other substances upon the crystallization of lactose. Browne⁷ states that sodium chloride, potassium acetate, and many other salts increase the solubility of sucrose and that "the presence of free alkali, and of different salts of the alkalies, increases the solubility of lactose in much the same manner as with sucrose." It is questionable, however, whether these salts are present in sufficient quantity in lactose products to affect materially the solubility of this sugar. Leighton and Peter⁸ have done work upon the factors which influence the crystallization of lactose. Hunziker and Nissen⁹ have investigated at 50° F and 65° F the effect of sucrose and milk colloids upon the solubility of lactose.

Before discussing the procedure and results embodied in this paper, which treats of the solubility determinations at 0°C and -3°C, it is perhaps advisable to consider the properties of sucrose and of lactose which have a bearing on their solubility relationships.

The very high viscosity of concentrated sucrose solutions at low temperatures¹⁰ is evident from Table I.

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TABLE I
Viscosity of sucrose in aqueous solution

| Temperature °C | Viscosity in centipoises Per cent sucrose by weight | | | |
|-------------------|--------------------------------------------------------|-------|-------|-------|
| | 0 | 20 | 40 | 60 |
| 0 | 1.7921 | 3.804 | 14.77 | 238. |
| 5 | 1.5188 | 3.154 | 11.56 | 156. |
| 10 | 1.3077 | 2.652 | 9.794 | 109.8 |
| 15 | 1.1404 | 2.267 | 7.468 | 74.6 |
| 20 | 1.0050 | 1.960 | 6.200 | 56.5 |

This high viscosity does not in itself affect materially the final solubility value of lactose in sucrose solutions but it does cause considerable experimental difficulty and, in a study of solutions at temperatures below their freezing points, it may so delay the normal equilibrium of the several phases that the correct value is obtained with difficulty. The influence of viscosity upon sucrose-lactose solubilities will be discussed more in detail in another section of this paper.

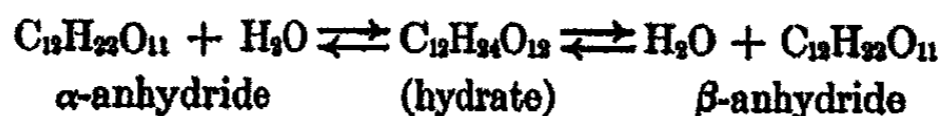
Lactose, likewise, evidences certain properties which prolong the time that is usually necessary for the determination of the solubility of a substance. The slow rate at which equilibrium is attained¹ is consequent to the existence in ordinary solution of two forms of lactose, namely, lactose hydrate and the β -anhydride. It is questionable whether a third form, α -anhydride, made by heating the hydrate crystals to 120°C, can exist in solution.

The normal form of lactose, which has been prepared by crystallization from water at ordinary temperatures, is lactose hydrate. In the presence of water this sugar dissolves to a definite value called the initial solubility,¹ and then is slowly converted into its equilibrium form, the β -anhydride. As this change proceeds more of the sugar (hydrate) dissolves until solution has reached completion. This value is spoken of as the final solubility.

If the β -anhydride, formed by crystallizing lactose above the transition temperature, 93°C, be dissolved, the reverse change β -anhydride \rightarrow lactose hydrate takes place. Thus solutions made from either form of lactose will exhibit the phenomenon of mutarotation and finally attain a constant value. This change may be measured in the polariscope.

The rate at which this equilibrium is attained is slow at 0°C, and increases with temperature; it is greatly accelerated by both hydrogen and hydroxyl ions, and the ratio of the rate of the reaction in 0.001 normal ammonium hydroxide solution to that in pure water is 2.4:1. At 75°C the equilibrium change is practically instantaneous and at temperatures below 93°C when equilibrium has been attained the ratio of lactose hydrate to β -anhydride is approximately 1:1.5.

By some investigators, however, it is assumed that the complete reaction equation, which is quite similar to the equilibrium equation which has been formulated for glucose, is:



Observations of this mutarotation reaction of lactose show that the laws of dynamics that hold for a simple unimolecular change are followed; hence the first part of the complete reaction which is thought to occur on dissolving lactose hydrate, namely, α -anhydride \rightleftharpoons hydrate, must take place instantaneously. Likewise the equilibrium between these two forms must be preserved.

That concentration, as well as temperature, has almost no influence on this equilibrium in solution is shown by the fact that there is no slow change in the rotatory power of milk sugar after dilution.

In addition to the investigations previously mentioned Urech¹¹ and Trey¹² have done work upon the influence of various substances on the rate of change of rotation of milk sugar. The latter in particular presents extensive data, covering a wide range of substances, on this mutarotation. Such observations are of special interest in relation to the rate of solution or of crystallization of lactose.

Thus sodium hydroxide (0.005N) and ammonia (0.05N) produce practically instantaneous equilibrium and in quite dilute solution these alkalies exert an accelerative influence on the rate of attainment of equilibrium. Hydrochloric acid in 0.4 normal solution establishes equilibrium quickly and in 0.04 normal solution accelerates the reaction. H-ions in equal concentration have less effect than OH-ions. Sucrose in a concentration of 17 grams per 100 cc. of solution exerts practically no effect. Very concentrated solutions at low temperatures, which more nearly approximate the conditions found in partly frozen ice cream and in condensed milk, however, have a viscosity which is approximately one hundred times greater and possibly exert considerable influence on the rate of attainment of equilibrium and on the equilibrium ratio.

In the measurement of lactose solubilities at 0° C and lower, values obtained by Hudson show that it is necessary to agitate the solutions in contact with the solute for a considerable length of time, and for a much longer time than at higher temperatures, in order to insure saturation. Thus the velocity constants of solution obtained by Hudson and calculated by the formula

$$k_2 = \frac{1}{t} \log_{10} \frac{S_{\infty}^H - S^H}{S^H - S_R}$$

were found to be:

$$0^{\circ}, 0.0125; 15^{\circ}, 0.0664; 25^{\circ}, 0.184.$$

Hudson obtained, both from supersaturation and undersaturation, values which were in reasonable agreement.

The velocity constants determined by Trey were of a somewhat different order. His constants were determined from the rate of change of the rotatory power of lactose solutions. It seems evident that the measurement of the constants by this change should give values in good agreement with

those determined from the maximum rate of solution or rate of crystallization because the surface of the solid in rate of solution and rate of crystallization experiments is so large, the stirring so rapid (and the temperature being low) that the actual process of solution or crystallization takes place very much faster than the controlling equilibrium change which precedes it, as measured by polariscopic readings. Hence a measurement of the change in rate of rotation should by calculation give velocity constants of the same magnitude as by determination from measurements of the rate of solution or of crystallization.

Trey, however, did not thus obtain values which can be said to be in reasonable agreement with those of Hudson. The constants of the former were calculated from the changing rotation values of lactose solutions according to the formula:

$$C = \frac{\log b - \log (b-x)}{t}$$

Comparison of this expression with that used by Hudson will show that in reality they are equivalent formulae.

The results of calculating the velocity constants of the two investigators to the same basis, giving the value of unity to the constant at 0°C, are as follows:

| | Rate of solution* | Hudson Rate of change of rotation | Trey Rate of change of rotation |
|-----|-------------------|--------------------------------------|------------------------------------|
| 0° | 1.0 | 1.0 | 1.0 |
| 15° | 5.3 | 5.85 | — |
| 20° | — | — | 8.57 |
| 25° | 15.5 | 15.6 | 10.15 |

*or rate of crystallization.

It seems evident that the values of Hudson are the correct ones. Not only were his determinations by the two independent methods in satisfactory agreement, but the rotation velocity constants, whether determined from lactose hydrate or anhydride solutions, were shown to be of the same magnitude. Such a result is predicted by theory and was verified by Roux.¹³ The rotation values (velocity constants) of hydrate and anhydride solutions as determined by Trey were not in good agreement.

Data have been obtained on the effect of sucrose and ammonium hydroxide on the magnitude of this velocity constant, the values being calculated from determinations made of the rate of crystallization of lactose from solutions containing these substances. This work will be presented in a later paper.

In reviewing past work it should be mentioned that the cryohydrate temperatures for the different forms of lactose as given by Hudson are of value in a study of lactose solubilities in partly frozen solutions.

An excellent review of lactose and its properties is given by Whittier.¹⁴

Experimental

The solubility determinations were made by enclosing an excess of the solid sugar with the respective sugar solution in ground glass stoppered bottles of approximately 125 cc. capacity. By means of spring clips the bottles were fastened upon a motor-driven metal frame, which revolved in an elec-

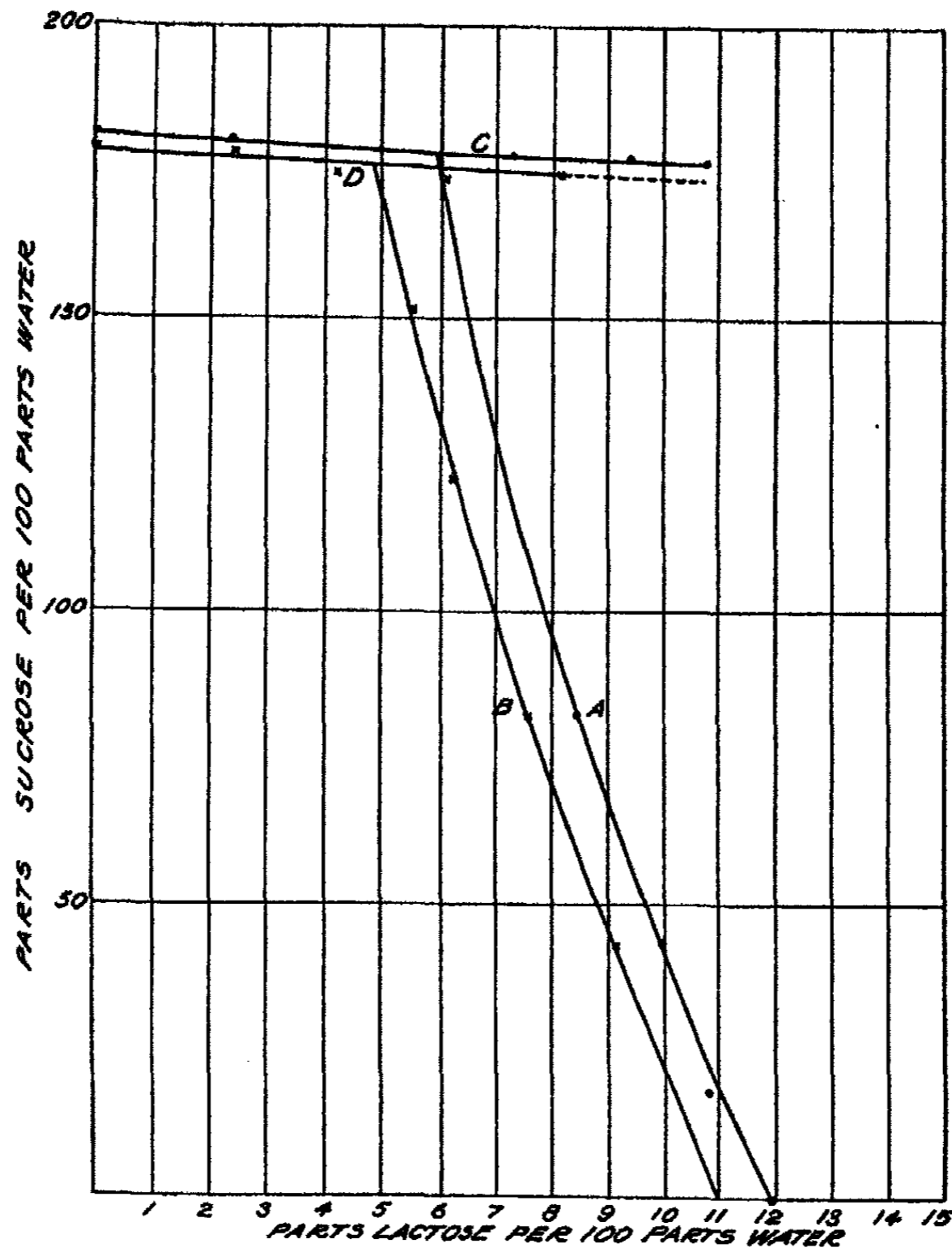


FIG. 1

Solubilities of lactose-sucrose solutions at low temperatures.

Curves A and C represent solubilities at 0°C
 Curves B and D represent solubilities at -3°C

trically-operated temperature-controlled bath. This bath was a water-alcohol-glycerine mixture which had a freezing point of approximately -10°C . The sugar solutions in which the solubility was to be measured ranged in concentration from 0.0% to approximate saturation and were, of course,

cooled to the necessary temperature before being added to the solid phase. Analysis by a method later described gave the exact concentration of these solutions. A small quantity of vaseline was placed upon the ground glass stoppers in order to make the bottles water-tight.

In all determinations at 0°C and below the solutions, in contact with an excess of the solid phase, were rotated for approximately 30 days. Duplicate samples were taken at time intervals of 7 days. The viscosities at low temperatures of some of the more concentrated sugar solutions were so high that equilibrium was but slowly attained.

In making the solubility measurements the bottles were removed from the metal frame and placed in a wire basket which was suspended in the bath. A short piece of rubber tubing was drawn over the end of a 1 cc. pipette and a small quantity of cotton was stuffed into it. Suction was applied at the other end. The tip of the pipette was placed just below the surface of the liquid to be sampled and 1 cc. of the solution was withdrawn.

The sample was placed in a tared weighing dish, the bottom of which was covered with a layer of asbestos. After being weighed, a small quantity of distilled water was added and the sample was evaporated to dryness at 105°C. It was further dried to constant weight in a vacuum oven. From this weight calculated on a water basis (parts total solids to 100 parts of water) was subtracted, likewise on a water basis, the concentration of the original solution. Such a determination gives the solubility of a sugar in 100 parts of water, in the presence of a definite concentration of another sugar.

In determining the solubilities in partly frozen solution it was necessary to use other methods of analysis. In these instances the methods of the

TABLE II

Solubilities of lactose in water and in sucrose solutions

| Kind of solution | Temperature | Solubilities of Lactose | | Solution used | |
|------------------|-------------|----------------------------------|--------------------|----------------------------------|--------------------|
| | | Parts lactose to 100 parts water | Percentage lactose | Parts sucrose to 100 parts water | Percentage sucrose |
| Water | 0°C | 11.94 | 10.68 | — | — |
| Sucrose in water | 0°C | 10.85 | 8.41 | 18.26 | 14.15 |
| " " | 0°C | 9.96 | 6.48 | 43.89 | 28.54 |
| " " | 0°C | 8.45 | 4.42 | 82.62 | 43.24 |
| " " | 0°C | 6.03 | 2.17 | 171.84 | 61.80 |
| Water | -3°C | Frozen | — | — | — |
| Sucrose in water | -3°C | 9.1 | 5.97 | 43.2 | 28.37 |
| " " | -3°C | 7.55 | 3.98 | 82.4 | 43.4 |
| " " | -3°C | 6.2 | 2.70 | 122.8 | 53.63 |
| " " | -3°C | 5.5 | 2.14 | 151.2 | 58.9 |

Association of Official Agricultural Chemists were employed. In all cases it was assumed that the form of lactose obtained on drying at 100° C was the anhydride. C. P. lactose and C. P. sucrose were used in this work.

TABLE III
Solubilities of sucrose in water and in lactose solutions

| Kind of solution | Temperature | Solution used | | Solubilities of Sucrose | |
|------------------|-------------|----------------------------------|--------------------|----------------------------------|--------------------|
| | | Parts lactose to 100 parts water | Percentage lactose | Parts sucrose to 100 parts water | Percentage sucrose |
| Water | 0°C | — | — | 181.69 | 64.5 |
| Lactose in water | 0°C | 2.40 | .85 | 180.23 | 63.8 |
| " " | 0°C | 4.88 | 1.72 | 178.8 | 63.0 |
| " " | 0°C | 7.32 | 2.57 | 177.75 | 62.4 |
| " " | 0°C | 9.43 | 3.29 | 177.48 | 61.9 |
| " " | 0°C | 10.82 | 3.76 | 176.36 | 61.45 |
| Water | -3°C | — | — | 179.0 | 64.2 |
| Lactose in water | -3°C | 2.40 | .85 | 178.5 | 63.5 |
| " " | -3°C | 4.2 | 1.50 | 175.0 | 62.7 |
| " " | -3°C | 6.1 | 2.18 | 174.0 | 62.1 |
| " " | -3°C | 8.2 | 2.89 | 175.5 | 61.9 |

Discussion

The data shown in Tables II and III and the values plotted in Fig. 1 represent the solubility relationships of lactose-sucrose solutions at 0°C and -3°C. It will be seen that the solubility of lactose in nearly saturated sucrose solutions is reduced to approximately one-half of its value in water. Consequently it appears that in ice cream, and likewise in condensed milk, particularly if it be subjected to low temperatures, the water may be greatly supersaturated with respect to lactose. Doubtless in the freezing of ice cream and its subsequent storage in the hardening room, as more and more water is converted into ice, a solution approximating saturation with respect to sucrose is obtained. Likewise the removal of water concentrates the lactose. These two factors tend to produce a solution which is highly supersaturated with lactose.

Whether or not the lactose will separate is, however, dependent upon other influences. Unpublished results which have been obtained show that the crystallization of lactose from viscous sucrose solutions is very slow. Hence, although the solubility of lactose is considerably less at the low temperatures of cold storage and the solution becomes supersaturated with respect to this sugar it will be seen that the very high viscosity at these temperatures of concentrated sucrose solutions creates an influence which opposes and materially

retards the separation of lactose. It may, therefore, require several weeks or even months for lactose to crystallize from solution.

For this reason it was advisable that the solubility determinations described in this paper be made from undersaturation and not conducted in such a way that equilibrium was attained from supersaturation.

Data by Jenkins³ serves to establish the above conclusion. He found that the determining factor which alters the velocity of crystallization is the viscosity of the solution. The relation is given by the expression

$$K = \frac{\text{Const.}}{n^{0.59}}$$

where K is the velocity constant and n is the viscosity.

It will also be seen that the presence of lactose has a slight effect on the solubility of sucrose. The two curves C and D which express this relationship cause the statements, with respect to the influence of viscosity upon the rate of crystallization of lactose, made in the preceding paragraphs, to appear more evident. Thus a solution which is approximately saturated with lactose can in turn become saturated with sucrose, and hence greatly supersaturate the solution with lactose, without the separation of the latter sugar during the interval of several weeks that the experiment is continued and the solution is agitated.

It thus appears that it is the viscosity of the solution and not the solubility of lactose which is the most important factor in controlling the separation of this sugar from concentrated sucrose solutions at low temperatures. Since, however, the viscosity of saturated sucrose solutions falls sharply as the temperature increases above 0°C, it seems very probable that with rising temperature the solubility of lactose will become the predominating influence upon lactose separation.

The results in Table III have also been expressed as percentages in order that they may be plotted in a triangular diagram expressing the phase rule relationships of the lactose-sucrose-water system. Such a representation will be made in a later paper when the cryohydrate relationships of the solutions and a more extensive temperature range have been studied.

Summary

The changes in the solubilities of lactose in sucrose solutions at 0° and -3°C are roughly inversely proportional to the concentrations of the sucrose and in approximately saturated sucrose solutions this solubility is reduced to about one-half of the solubility value in water.

Owing to the limited solubility of lactose in water at 0° and -3°C the solubility of sucrose at these two temperatures is but little affected by the presence of lactose. The values bear an inverse relationship to the concentration of the lactose in solution.

Lactose in the presence of high concentrations of sucrose may be very supersaturated with respect to the solution and yet, because of the high viscosity, crystallize very slowly.

The relationship of the above conclusions to the crystallization of lactose in several dairy products has been discussed.

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THE RATE OF THE MULTIPLICATION OF YEAST AT DIFFERENT TEMPERATURES*

BY OSCAR W. RICHARDS

Changes in the rate of multiplication of yeast¹ that accompany changes in the temperature of the culture medium are masked, in the usual test tube culture, by the toxic effect of the products of their metabolism on the yeast cells. These excretions injure the larger buds and the population gradually reaches an equilibrium number². Consequently, the apparent effect of temperature becomes progressively less as the equilibrium of the population approaches.³ The influence of temperature on the multiplication of yeast, uncomplicated by the inhibitory action of the excretion products, can be measured only during the period during which the rate of growth is constant and the retarding effect of the toxic excretion products is circumvented.⁴

Unless the culture medium is changed at sufficiently frequent intervals to maintain it effectively constant, only the first part of the growth cycle is usable, as the growth rate begins to decrease at about 30 hours after seeding. During this period the numbers of cells present are less and the errors of counting are higher. The technical difficulties involved in properly renewing the culture medium prevented the use of longer growth periods in this investigation.

I.

The method of culturing the yeast and making the counts has been described elsewhere⁵. A pure strain of *Saccharomyces cerevisiae* Hansen was used. When the logarithm of the number of cells present in a unit sample of the culture medium is plotted against time, the resulting graph is a straight line, within the experimental error, for periods of time extending from 1 to 2 hours after seeding until about 30 hours. After a lag period of less than 2 hours the rate of growth is constant. A similar lag period is described by Slator.⁶ The effect of this short latent period is minimized in the experiments, as only the linear part of the curve was used in making the measurements. A lag period would merely shift the position of the growth curve further from the origin on the time axis. A long lag period would delay the time of reaching the equilibrium population, but would not affect the numerical value of the

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¹ These experiments will be designated as those made at Worcester and Cambridge. The yeast is the same in both cases except that a single cell of the yeast used at Cambridge was isolated and the yeast used in the Worcester experiments belongs to the pure line started by this cell.

² Richards: Bot. Gazette (1928).

³ Richards: Ann. Bot., 42, 271 (1928).

⁴ Richards: J. Gen. physiol., 11, 525 (1928).

⁵ Biochem. J., 12, 248 (1918).

⁶ Slator: J. Gen. physiol., 11, 525 (1928).

equilibrium level. This relation has been shown by Lotka¹ in connection with his treatment of the dynamics of an epidemic of malaria. At a definite stage during an epidemic there is reached an equilibrium between the population of malarial organisms and the infected human population. In this case Lotka has shown that the incubation period (a lag period) has only a constant effect on the equilibrium because the lag period merely slows down somewhat the progress of the events in the system.

The cultures of the experiments at temperatures below room temperature were made by immersing the tubes in a light-tight box in a constant-temperature thermostat of the type described by Crozier and Stier,² or in a small beaker of water in a Kelvinator.³ The other cultures were maintained in either a Freas or Thelco incubator.

Two measures of the rate of multiplication were used: the slope of the growth curve, and the reciprocal of the time required by the culture to produce a definite number of cells. The latter was obtained by determining the time of intersection of the growth curve and a line corresponding to antilog 0.50 cells.

Technical difficulties make it impractical to seed each set of tubes with exactly the same number of cells. The rate of growth of yeast also varies with the age of the seeding. Even with seedings of nearly the same age there is some normal variation in the rate of multiplication. The best method for minimizing these variations seemed to be to grow a control set with each experimental set and to adjust the curves so that all of the controls had the same rate of growth. The controls were maintained at 30°C. Should this experiment be repeated the control temperature should be preferably about 2° to 4° lower in order to obtain more uniform growth at the "control" temperature (cf. Sec. IV).

To minimize the variations, the growth curves for each control and for the corresponding set of data at each temperature were plotted on tracing paper and the intercept of the growth curve of the control and the line of antilog 0.50 was marked. Another graph had a line drawn which was the most representative of all of the control growth rates and the line of antilog 0.50 was drawn on this graph. Then each of the sets on tracing paper was placed on this master graph and the growth line of the control made to coincide with the line of the master graph. The slopes and intercepts for the experimental sets were then measured on the master graph.

II.

The rate of growth is expressed as the tangent of the angle that the growth curve makes with the time axis. These rates may be conveniently plotted as the logarithm of the tangent against the reciprocal of the absolute temperature, as in Fig. 1. A straight line then expresses the relation between the

¹ Am. J. Hyg., Jan. Supplement (1923).

² J. Gen. Physiol., 10, 501 (1927).

³ The Kelvinator was loaned to me for these experiments through the courtesy of the Worcester Electric Light Company.

rate of multiplication of the yeast and the temperature between about 9° and 29°C. with the exception of the observation at 10°. Another straight line expresses this relation between 9° and 4°

The divergence of the measurement at 10° from the others seems to be due to hysteresis. To avoid this effect it is necessary that the yeast used at

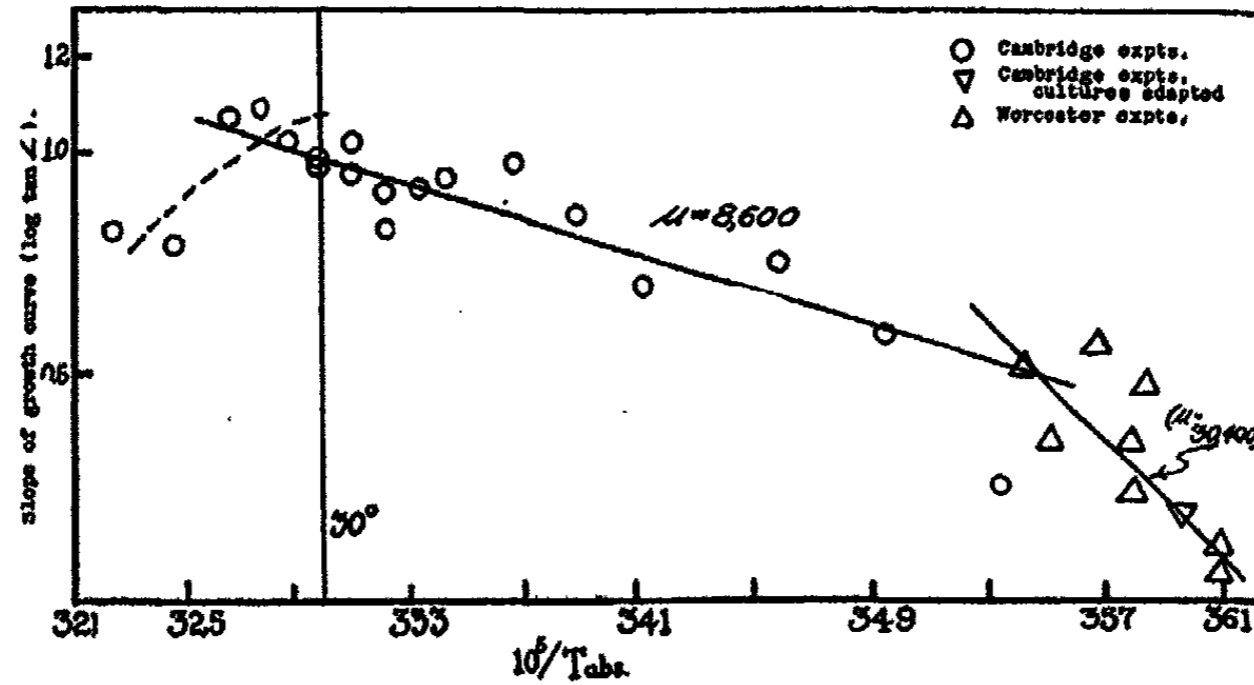


FIG. 1

Rate of multiplication of yeast measured by the slope of the growth curves.

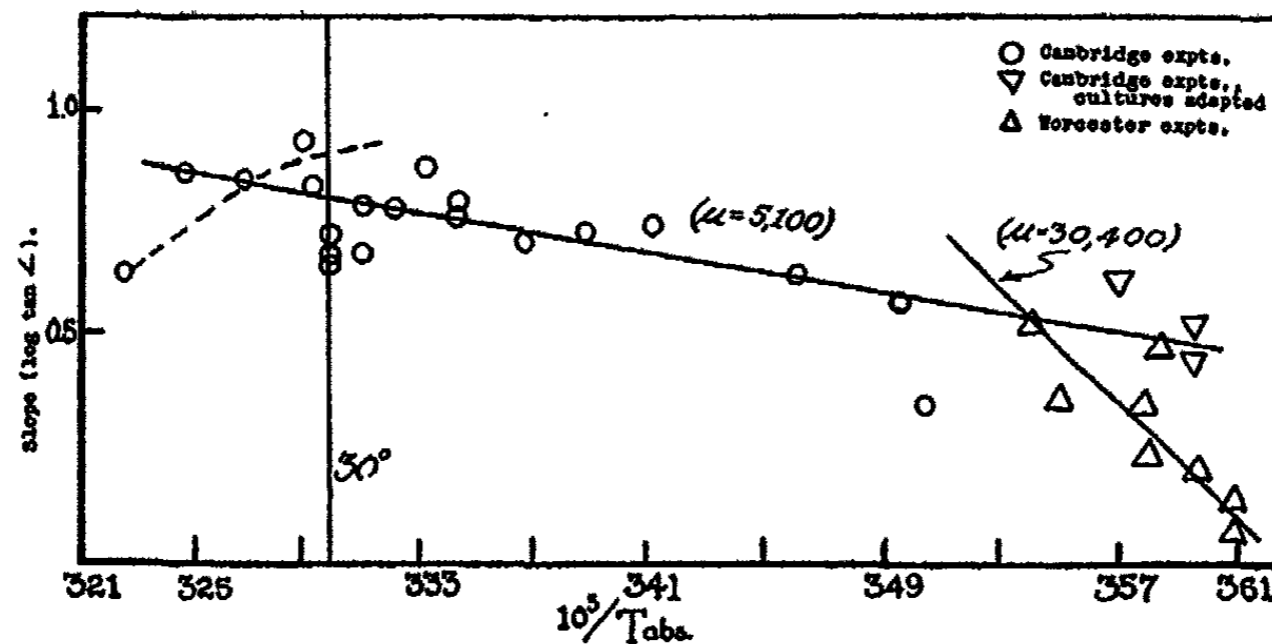


FIG. 2

Rate of multiplication of yeast measured by the slope of the growth curves. Same as Fig. 1, except that the variation in the different series is not minimized by adjusting the rates of growth of the controls to be the same (cf. note in text).

the lower temperatures be first well adapted to the particular temperature of the experiment. When the yeast is properly adapted the rates are higher and more self-consistent. In the experiments in which the cultures were adapted to the temperature the adaptation period was 7 days for the Cambridge experiments and 10 days for the Worcester experiments.

Above 30° the rates decrease in an accelerated manner. This is partly due to certain cells being selectively destroyed and partly due to some effect of the nature of a thermal destruction. When these two effects are measured separately it will probably be possible to determine the nature of the thermal destruction by a method similar to that used by Hecht¹ for a somewhat analogous case. This effect is shown more clearly by the other measure of the rate of cell proliferation discussed in the next section.

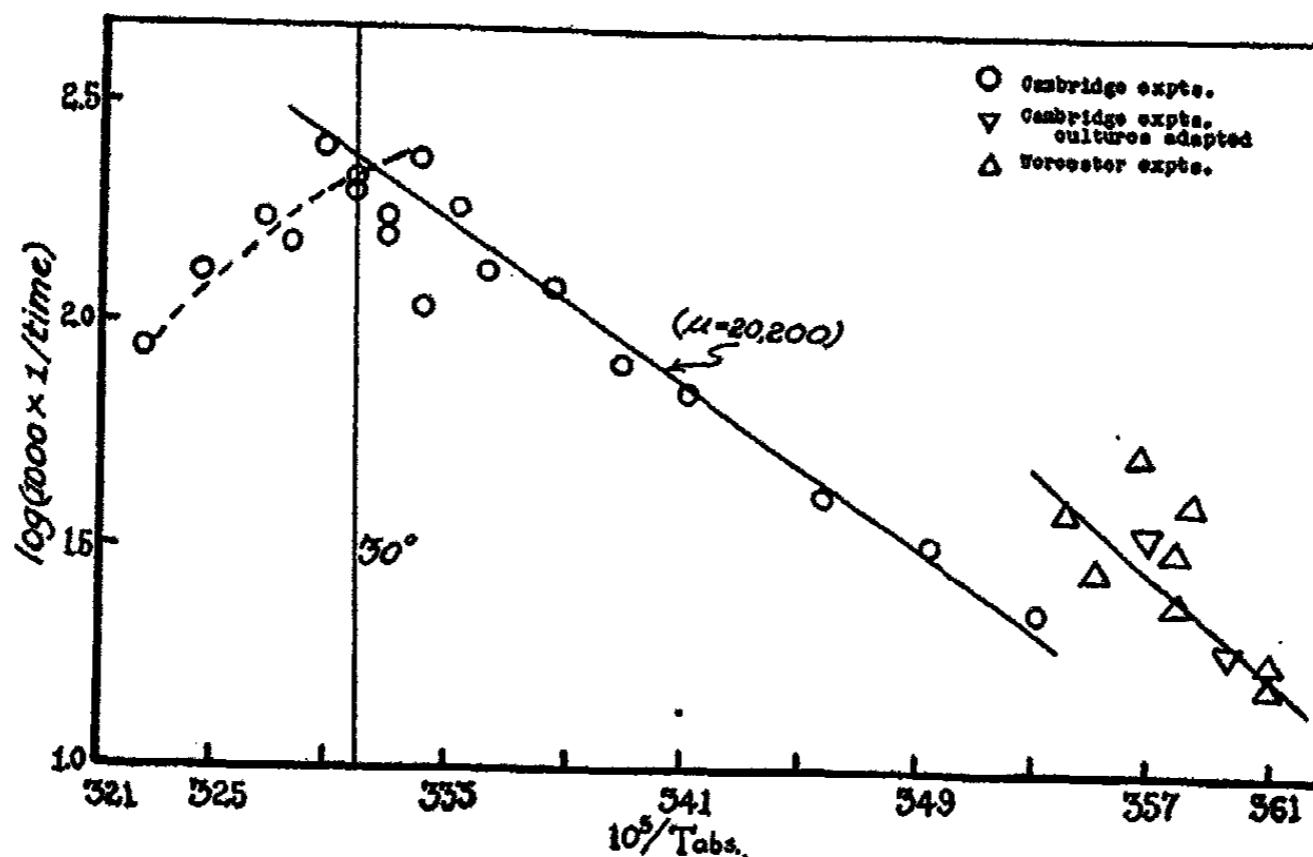


FIG. 3

Rate of multiplication of yeast measured by the reciprocal of the time required to produce a given crop.

The changes in the trends of the rates are also shown if the slopes of the original growth curves are used without minimizing the variations of averaging the rates of the controls, as is shown by Fig. 2. The increment in this figure has probably no really exact meaning; it might be suggested as a case where faulty interpretation gives a non-significant μ . The rates for the lower temperatures are the same in both figures, as when the yeasts are adapted at a given temperature it is no longer possible to maintain a strictly comparable control at a higher temperature. Thus the regions at 9° and 30° seem to be critical temperatures; they occur at regions that have been emphasized by Crozier² as significant in this respect. The scattering of the velocities around 30° seems to indicate a real "break" in the curves of the velocities, rather than an effect of the chemical constituents of the medium varying with the temperature, as suggested by Sherwood and Fulmer.³

¹ J. Gen. Physiol., 1, 667 (1918).

² J. Gen. Physiol., 9, 525 (1926).

³ J. Phys. Chem., 30, 738 (1926).

The decrease in the rate of growth at temperatures higher than 30° suggests that budding would cease at about 44°, which is in accordance with the observations gathered by Guilliermond¹ with various yeasts.

III.

The measurements from the other criterion of the rate of growth may be exhibited in a similar manner, by plotting the logarithm of the reciprocal of the time to yield a certain crop against the reciprocal of the absolute temperature, Fig. 3. This graph shows the same features as the previous figures. The different slopes of the curves of the velocities in Fig. 3 from those of Fig. 1 are probably due to the fact that the length of the lag period varies with the temperature. A change in the lag period would change the time of the intercept of the growth curve and the line of antilog 0.50 cells. Consequently these measurements contain the effects of temperature on both the lag period and the rate of growth. This effect, which was obviated by the method used in Section II, makes the rates of Fig. 3 less reliable than those of Figs. 1 and 2 and prevents obtaining a good fit or a significant increment. Strumia and McCutcheon² find variations in the length of the lag period for their measurements of larger amounts of yeast for the first nine hours of growth. Large seedings permit more precise measurements of the lag period, but the greater amount of excretion products shortens the time during which multiplication occurs at a constant rate. Until the technical difficulties incident to keeping large seedings of yeast growing at a constant rate are overcome it will not be possible to separate the effect of temperature on the lag period from the effect of temperature on cell proliferation.

The numerical values obtained by solving the Arrhenius temperature equation³ for each group of data are given on the figures. In general these values correspond with the classes of values found for growth processes,⁴ but the present values are for *cell multiplication* during the increase of a population and they are not to be compared directly with these for growth of a multicellular organism or the elongation of an unicellular organism. Values of the critical increment of the Arrhenius equation that may be used for analytical purposes can only be obtained when the causes of variation mentioned in this paper are adequately controlled.

IV.

It is possible to locate more precisely the upper critical temperature for the multiplication of yeast by studying the changes in the form of the cells.

¹ "Les Levures" (1912).

² From unpublished manuscript communicated personally to the writer.

³ The Arrhenius equation is

$$k_1/k_2 = E^{\frac{\mu}{R}}(1/T_1 - 1/T_2)$$

when k_1 is the velocity, or proportional measure of it, at the temperature T_1 , and k_2 the corresponding velocity at the temperature T_2 . The temperatures must be expressed in the absolute or Kelvin scale. When only approximate values of μ are desired, they may be obtained from a nomogram, Richards: J. Phys. Chem., 30, 1219 (1926).

⁴ Crozier: J. Gen. Physiol., 10, 53 (1926); Castle: 11, 407 (1928).

Irregular elongate cells are occasionally seen in cultures incubated at 30°C. at from 10 to 30 hours after seeding. Later these cells are not found, and as the strain used is pure and the technic known to be adequate to prevent infection, it seemed necessary to see if their occurrence was associated with certain temperatures. Cells that occasionally infest a tube accidentally are different from these abnormal forms both in shape and size. The bizarre cells resemble more those cells seen in very old cultures or in cultures maintained at high temperatures.¹

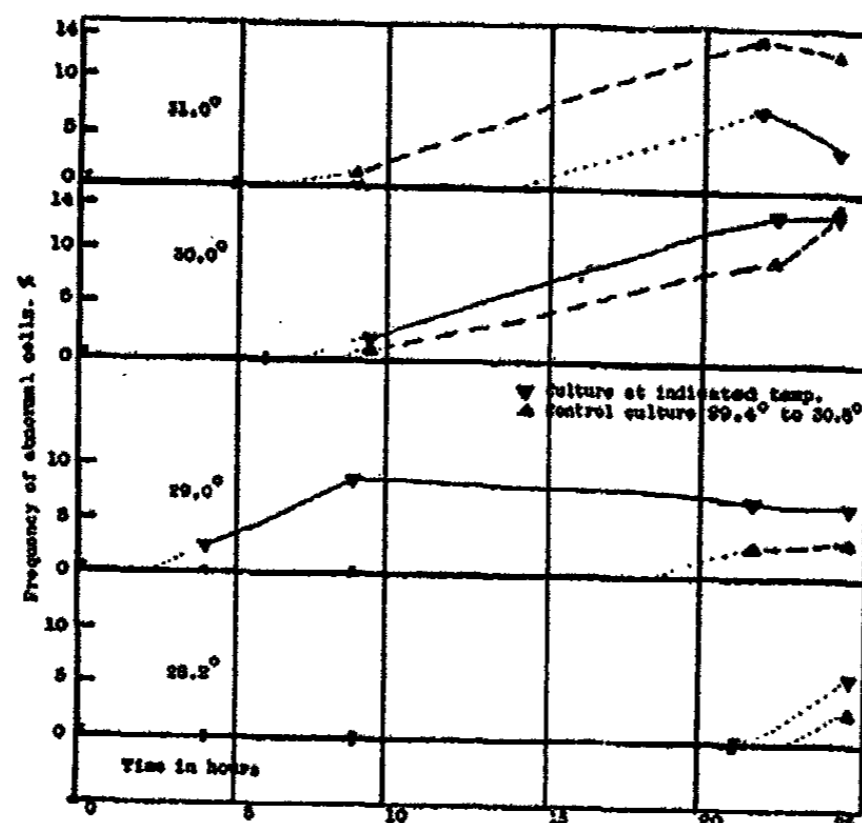


FIG. 4

The frequency of the occurrence of the abnormal cells described in the text (cf. Fig. 5, b).

Four experiments were made by growing a series of tubes at temperatures from 28° to 32° and by determining the frequency of these abnormal cells. The incubator containing the controls varied about $\pm 0.7^\circ$, but the water thermostat in which the experimental tubes were grown varied only a few hundredths of a degree. This permitted comparing the cells grown in the usual laboratory incubator having fair temperature control with a group grown at more adequately controlled temperatures. The results are expressed in Fig. 4. The difference in shape between the usual form of *S. cerevisiae* and these abnormal forms is shown in Fig. 5. The drawings are tracings of enlarged photomicrographs made by the method described elsewhere².

Up to and including 30° we find more abnormal cells in the group grown in the water thermostat. At 30° the frequencies are approximately equal, and at 31° the frequencies are exactly reversed. At a temperature maintained between 29.5° and 30.5° more of these unstable, morphologically different cells appear, which suggest that this is a critical temperature which

¹ Guilliermond: "Les Levures" (1912).

² Richards: Bot. Gazette (1928).

disturbs the budding process. This effect does not change the constancy of the rate of multiplication of the yeast. A temperature of 30 degrees has been shown to be accompanied by critical effects in various kinds of vital activities.¹

V.

The existence of such a critical temperature for the growth of yeast is of great importance, because the temperature of 30° is customarily used as a normal temperature in the study of the vital activities of yeast. This critical temperature may not be the same for all strains of the same species of yeast, and it is possibly different for different species.

The unusual forms are not of frequent occurrence unless the temperature is maintained constant within narrow limits, which is not achieved by the types of laboratory incubators in most general use at the present time. The better types of temperature control which will come with wider use of adequate thermostats makes a thorough knowledge of these special temperature zones prerequisite for the study of the metabolism of yeast and similar organisms, as well as

constant conditions of culture medium. It is possible that this special effect of temperature at which investigations using yeast are frequently made may be responsible for part of the irregularities apparent in the published accounts of such studies. This is particularly true for the investigations that are primarily concerned with the first 24 hours growth after seeding, because it is during this period that the budding process is most sensitive to effects associated with certain temperatures. During later growth the effect of temperatures is hidden by the greater effect of the waste products secreted by the yeast on the rate of increase of the yeast population.

The writer wishes to express his indebtedness to Dr. W. J. Crozier for helpful suggestions and friendly criticism during the progress of these experiments.

Summary

The rate of the multiplication of the yeast *Saccharomyces cerevisiae* increases regularly with increase of temperature between 4° and 30°, except that the rate of change alters at 9°. Above 30° a decrease in the rate of growth is associated with an increase in temperature. At 30°C. abnormal, elongate cells are produced which indicates that this temperature effects the process of bud formation in a critical manner. More of these abnormal cells appear if the temperature is maintained within narrow limits of variation. The need for precise control of the temperature of yeast cultures is emphasized.

¹ Crozier: J. Gen. Physiol., 9, 525 (1926).

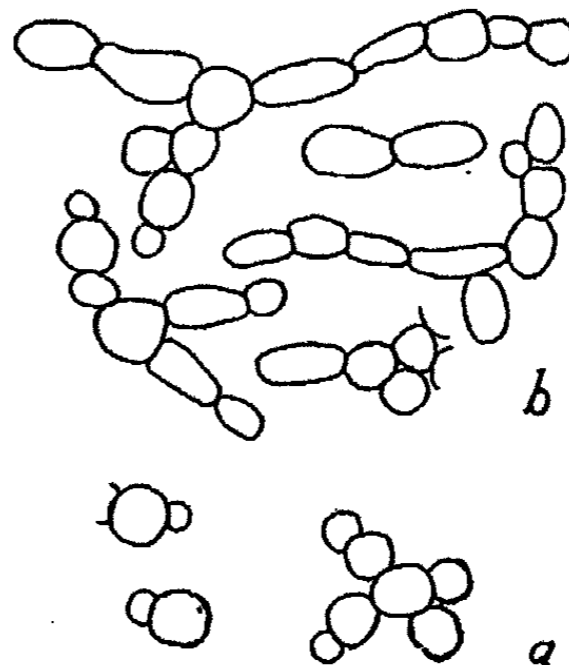


FIG. 5
a, Normal cells.
b, Abnormal cells.

THE EFFECT OF NON-ELECTROLYTES ON THE STABILITY OF COLLOIDS. II

Ferric Hydroxide Sol

BY SUBODH GOBINDA CHAUDHURY AND ASHUTOSH GANGULI

Introduction

In Part I¹ it has been pointed out that in general the addition of a non-electrolyte brings about a change in the dielectric constant and also in the interfacial tension. The change in the dielectric constant will bring into play²:

- (1) greater repulsive forces between the colloidal particles,
- (2) increased electrical adsorption of precipitating ions,
- (3) a diminution in osmotic coefficient of the electrolyte.

It has been pointed out that, as the presence of non-electrolytes lowers the surface tension, adsorbability and coagulating power cannot go hand in hand, as is frequently assumed by workers in this field. In this paper, the behaviour of ferric oxide sol in presence of methyl and ethyl alcohols, sugar, urea, glycerol, and pyridine has been studied. Measurements of charge under these conditions are in progress; only the coagulating concentrations of different electrolytes will be given in this paper.

Freundlich and Rona³ found that the presence of non-electrolytes sensitises a ferric oxide sol. They also measured the cataphoretic velocities of ferric oxide sol in presence of camphor and thymol and found them to be lower than the value of the pure colloid. Weiser has carried out both adsorption and coagulation experiments with ferric oxide sol in presence of phenol and iso-amyl alcohol. He remarks that "the precipitation concentration of KCl is lowered a small amount by the presence of a non-electrolyte while that of salts with multivalent precipitating ions is changed but little if at all." From these observations he concludes that "we should expect phenol and isoamyl alcohol to have little influence on the adsorption of multivalent ions during the precipitation of colloidal oxides." From the theoretical considerations set forth in Part I, we have seen that adsorption as measured analytically and coagulating power should not necessarily go hand in hand.

Experimental

The sol was prepared by peptising freshly precipitated ferric hydroxide with a solution of ferric chloride and then dialysing the sol till the dialysate gave no test for iron. Coagulation experiments were performed in such a way

¹ J. Phys. Chem., 32, 1481 (1928).

² Mukherjee and Chaudhury: J. Indian Chem. Soc., 2, 3, 7, (1925); Indian Science Congress (1927).

³ Biochem. Z., 81, 87 (1917).

that the precipitate settled down within five minutes leaving a clear supernatant liquid above .5 c.c. of the sol were mixed with 5 c.c. of mixtures of electrolyte and water. Tables I-VI contain the experimental results:—

TABLE I

Ferric hydroxide sol and methyl alcohol.

| % Methyl alcohol by volume | KCl $N \times 10^{-3}$ | K_2SO_4 $N \times 10^{-4}$ | $K_3Fe(CN)_6$ $N \times 10^{-4}$ |
|-------------------------------|---------------------------|---------------------------------|-------------------------------------|
| 0 | .827 | 3.3 | 2.5 |
| 10% | .827 | 2.8 | 2.35 |
| 20% | .702 | 2.6 | 2.07 |
| 25% | .652 | 2.5 | 2.00 |

TABLE II

Ferric hydroxide sol and ethyl alcohol.

| % of ethyl alcohol | KCl $N \times 10^{-3}$ | K_2SO_4 $N \times 10^{-4}$ | $K_3Fe(CN)_6$ $N \times 10^{-4}$ |
|-----------------------|---------------------------|---------------------------------|-------------------------------------|
| 0 | 1.35 | 3.59 | 2.70 |
| 10% | 1.20 | 3.2 | 2.60 |
| 20% | 1.00 | 2.88 | 2.45 |
| 25% | 0.85 | 2.74 | 2.45 |

TABLE III

Ferric hydroxide sol and pyridine.

| % Pyridine | KCl $N \times 10^{-3}$ | $K_3Fe(CN)_6$ $N \times 10^{-4}$ |
|------------|---------------------------|-------------------------------------|
| 0 | 1.55 | 2.75 |
| 0.005 | 1.50 | 2.70 |
| 0.010 | 1.45 | 2.6 |
| 0.020 | 1.304 | 2.50 |

TABLE IV

Ferric hydroxide sol and urea.

| % Urea (saturated sol) | KCl $N \times 10^{-1}$ | K_2SO_4 $N \times 10^{-3}$ | $K_3Fe(CN)_6$ $N \times 10^{-4}$ |
|---------------------------|---------------------------|---------------------------------|-------------------------------------|
| 0 | 5.00 | 3.44 | 4.39 |
| 2.5 | 4.9 | — | — |
| 10.0 | 4.4 | 4.05 | 3.5 |
| 25.0 | — | 4.2 | 2.7 |

TABLE V

Ferric hydroxide sol and cane sugar.

| % of cane sugar. (100 gms in 1 litre) | KCl $N \times 10^{-1}$ | K_2SO_4 $N \times 10^{-3}$ | $K_3Fe(CN)_6$ $N \times 10^{-4}$ |
|------------------------------------------|---------------------------|---------------------------------|-------------------------------------|
| 0 | 5.00 | 3.44 | 4.39 |
| 10% | 5.00 | 3.85 | 4.08 |
| 25% | 5.2 | 3.57 | 3.87 |

TABLE VI

| % Glycerol | Ferric hydroxide sol and glycerol. | | |
|------------|------------------------------------|---------------------------------|-------------------------------------|
| | KCl $N \times 10^{-1}$ | K_2SO_4 $N \times 10^{-4}$ | $K_3Fe(CN)_6$ $N \times 10^{-4}$ |
| 0 | 5.00 | 3.50 | 4.39 |
| 10 | 4.7 | 3.44 | 3.92 |
| 20 | 4.8 | 3.37 | 3.67 |
| 25 | 5.00 | 3.37 | 3.67 |

Discussion

Methyl and ethyl alcohol and pyridine always sensitise the sol independently of the valency of the precipitating ions. These non-electrolytes possess lower dielectric constants than water and consequently a greater number of precipitating ions and lower number of similarly charged ions will be adsorbed for the same concentration of the electrolyte (Part I. loc. cit.). The behaviour of urea, cane sugar, and glycerol is not so regular; urea sensitises the sol towards potassium chloride and potassium sulphate. Glycerol sensitises the sol towards potassium sulphate and potassium ferrocyanide; towards potassium chloride it first sensitises but with higher percentages of glycerol, the coagulating concentration of the electrolyte attains its original value. It has been shown by Mukherjee, Chaudhury and Mukherjee that ethyl alcohol shows by far the larger number of instances of stabilisation against coagulation by electrolytes in the case of arsenious sulphide sol. It thus appears that the effect of a non-electrolyte depends on the nature of the hydrosol taken. The above tables also confirm that the valency of the precipitating ions, as such, has no effect on sensitisation or stabilisation of sols in presence of non-electrolytes, as assumed by Kruyt and van Duin in the case of arsenious sulphide sols. In cases of alcohol and pyridine therefore, the effect of the dielectric constant seems to be the dominant factor. The dielectric constant of urea solutions is greater than that of water and therefore we should expect greater stabilisation. Surface tension data being not available we are unable to discuss the point further. It may be remarked that urea being a weak base will combine with HCl present in the $Fe(OH)_3$ sol. This will sensitise the sol. The surface tensions and dielectric constants of solutions of sugar are slightly less than those of the pure solvents at the concentrations taken.

Our best thanks are due to Prof. J. N. Mukherjee, D.Sc., for his advice and for facilities for work.

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THE PHYSICAL CHEMISTRY OF COLOR LAKE FORMATION. IV
RED CONGO ACID AND CONGO RED LAKES

BY HARRY B. WEISER AND ROBERT S. RADCLIFFE

Congo red, the disodium salt of diphenyl-disazo-bis-naphthylene-4-sulfonic acid is a red dye substantive to cotton. From osmotic pressure measurements on the dye solution using a parchment membrane, Bayliss¹ obtained a molecular weight 88 to 97 percent of the theoretical value, 696. Similar observations by Biltz and Vegesack² and by Donnan and Harris³ would indicate that the salt dissolves in the form of undissociated molecules. Conductivity measurements on the solutions indicate, however, that the salt is practically completely dissociated; but if this were the case, the osmotic pressure should be twice as large and the molecular weight half as large as the values actually obtained. To account for the conflicting observations, Biltz assumed that the particles have a molecular weight which is a multiple of the simplest value, the experimental value between 600 and 700 resulting from dissociation. In line with this, Herzog and Polotsky⁴ found the diffusion constant of Congo red to be 0.126×10^{-6} at 6.9° which is considerably smaller than would be expected if the molecular weight were but 696. For example, erythrosin B with a molecular weight of 800 and with 37 atoms instead of 70 for Congo red, has a diffusion constant of 0.265×10^{-6} at 6.6° . An apparent objection to assuming that the dye anions are associated is that the high conductivity of the salt would require large ions to have a relatively large migration velocity, contrary to what one might expect, *a priori*. This difficulty disappears in the light of McBain's⁵ observations on soap solutions. The anions in such solutions were found to be colloidal ions or ionic micelles (aggregates of simpler ions) possessing a mobility of the order of magnitude of that for the potassium ion. The slow migration velocity of large ions such as palmitate is due to its one electron being insufficient to charge up the ion to the surface density necessary for the average mobility. On the other hand, with the aggregates of ions, the ratio of the number of charges to the size, is such that the particles may possess a mobility even larger than the average.

The colloidal nature of the Congo red anion is indicated by its very small diffusion into gelatin⁶ and its failure to dialyze⁷ through parchment or col-

¹ Proc. Roy. Soc., 81 B, 269 (1909); 84, 229 (1912).

² Z. physik. Chem., 73, 481 (1910).

³ J. Chem. Soc., 99, 1554 (1911).

⁴ Z. physik. Chem., 87, 449 (1914).

⁵ J. Soc. Chem. Ind., 37, 249 T (1918); McBain, Laing, and Titley: J. Chem. Soc., 115, 1279 (1919); McBain and Salmon: J. Am. Chem. Soc., 42, 426 (1920); Proc. Roy. Soc., 97 A, 44 (1920).

⁶ Herzog and Polotsky: Z. physik. Chem., 87, 449 (1914).

⁷ Teague and Buxton: Z. physik. Chem., 60, 479 (1907); Vignon: Compt. rend., 150, 619 (1910).

lotion. This is further evidenced by the following ultrafiltration experiment: Aqueous solutions of Congo red containing 0.025, 0.05, and 1 gram, respectively, of the purified salt per liter were filtered through a cellophane membrane ultrafilter under approximately 7 atmospheres pressure. The filtrate was perfectly clear in every case, but was slightly alkaline owing to partial hydrolysis of the salt forming the non-filterable blue colloidal acid, and alkali which will pass the membrane. These observations taken together with the dialysis experiments are quite indicative of the colloidal nature of the anion. The only other way of accounting for the failure of the anion to pass the membrane is to assume that the cellophane is acting as a semipermeable membrane and not as a sieve. This would mean that the membrane must show sufficiently strong negative adsorption for the Congo red anion to fill the pores with water. Actually the dye is adsorbed by the membrane. A further possibility is that the dye-cellophane adsorption complex shows strong negative adsorption for Congo red just as the copper ferrocyanide-potassium ferrocyanide adsorption complex exhibits negative adsorption for ferrocyanide and so prevents its passage under certain conditions.¹ This possibility is ruled out, however, on the ground that the adsorption of an ion must be practically irreversible or the adsorption complex cannot act as a semipermeable membrane for the ion in question. This is approximately true for the adsorption of ferrocyanide by copper ferrocyanide from solutions below 1 normal, but is by no means true for the adsorption of Congo red by cellophane. There is, therefore, little doubt but that the red anions of Congo red are colloidal micelles or aggregates of single ions, too large to pass a fine ultrafilter and too hydrous and fine to be visible in the ultramicroscope.

The solution of the red sodium salt becomes violet at a pH value of 4 and blue at a pH value of 3.² The blue color is due to a quite insoluble blue acid formed by replacing the sodium of the salt with hydrogen. This blue acid can form a stable negative sol containing particles sufficiently large and anhydrous to be visible in the ultramicroscope.

The Red Congo Acid

In addition to the blue Congo acid Schaposchnikoff and Bogojawlenski³ claim to have prepared a red acid by dissolving the solid blue acid in pyridine, evaporating, and heating the resulting salt at 120° to drive off the pyridine. Hantzsch⁴ points out that the acid prepared in this way is not red but is reddish brown and, in compact mass, a dark brown-violet color. The blue acid is reported to be quite soluble in alcohol and acetone giving stable solutions of the red acid. Hantzsch reports also that heating a dilute blue sol in a platinum or quartz dish sometimes causes it to turn to a red which reverts to the original blue on cooling.

¹ Weiser: "The Colloidal Salts," 283 (1928).

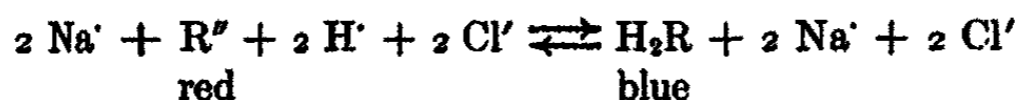
² Salm: *Z. physik. Chem.*, 57, 471 (1906).

³ *J. Russ. Phys. Chem. Soc.*, 44, 1813 (1913).

⁴ *Ber.*, 48, 158 (1915).

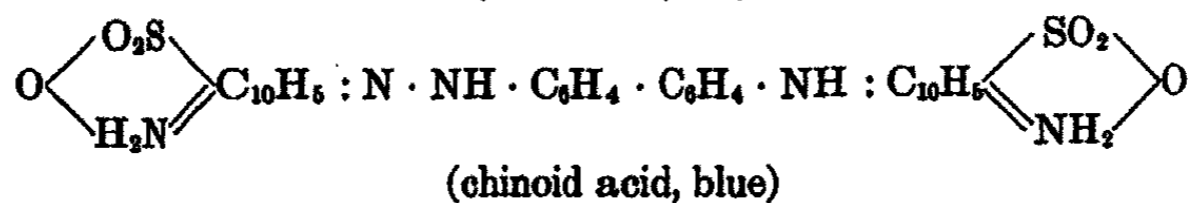
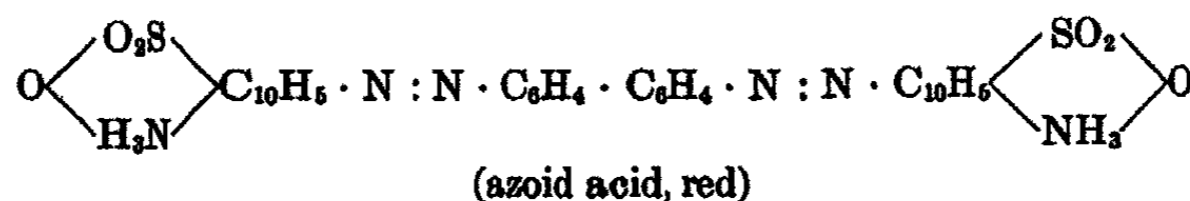
The effect of the nature of the solvent on the color change was shown by Hantzsch¹ in the following way: Thirty cubic centimeters of 0.0004 molar salt was diluted with 250 cc of liquid. If water was used the solution was turned to blue by 6 cc of N/10 alcoholic HCl whereas if alcohol was used the solution was red after the addition of 15 cc of N/10 alcoholic HCl and did not change to blue for 3 to 5 minutes.

As indicated above, the first transformation in color on adding dilute acid to Congo red is from red to purple or violet. The equation for the reaction may be represented as follows, R^{''} standing for the Congo red anion.



Hantzsch observed, however, that when equivalent amounts of salt and acid are brought together in dilute solution, the color is purple and not blue. This purple color is believed by Hantzsch to be a mixture of red and blue acid; but this does not follow necessarily since the reaction indicated above is probably reversible to a certain extent. Indeed, Michaelis and Rona² found that neutral salts change the violet-colored solution to red. Similarly, Kolthoff³ showed that an N/50 solution of sulfuric acid saturated with sodium chloride is colored red by Congo red and not blue as it is in the absence of salt. Furthermore, a one percent solution of sodium chloride renders Congo red useless as an indicator in acidimetry. Wedekind and Rheinboldt⁴ observed that a violet solution prepared as described above turns red on heating and becomes violet again on cooling. Here also, one cannot say to what extent this is due to the formation of red acid and to what extent to reversal of the reaction with the formation of more of the red anion derived from the salt.

Hantzsch is of the opinion that the color changes of all indicators are due to change in structure. He concludes therefore that the red and blue acids are the azoid and chinoid forms, respectively, of the following formulas:



The only evidence for this difference in structure is a variation in the visible portion of the absorption spectrum of solutions obtained when equivalent amounts of Congo red and sulfuric acid are mixed (1) in aqueous solution and (2) in alcoholic solution.

¹ Ber., 48, 158 (1915); cf., also, Kolthoff: Rec. Trav. chim., 42, 251 (1923).

² Z. Elektrochemie, 14, 251 (1908).

³ Chem. Weekblad, 13, 284 (1916); Rec. Trav. chim., 42, 251 (1923).

⁴ Ber., 52, 1013 (1919).

Since the color of metallic sols such as gold is determined in part by the size of the particles, Wo. Ostwald has proposed a theory of color change in indicators based on change in the degree of dispersion of colloidal particles. Thus Ostwald¹ showed that the color change from red to blue in Congo rubin sol is produced by almost all electrolytes and that the effect of ions of different valency on the change is similar to that on typical hydrophobic sols. From these observations, he concludes that the color changes of Congo red are likewise due to differences in dispersion. Wo. Ostwald's theory is not accepted² generally although it is recognized that degree of dispersion may influence the color, in certain instances. But with indicators such as Congo red, litmus, phenolphthalein, etc., where the color is so closely related to the hydrogen ion concentration and is so little dependent on other ions, it seems a very remote possibility that change in dispersion is the only factor coming in. Indeed, Haller³ is of the opinion that the change of color of Congo rubin with acids is not the same in nature as that with salts.

Experimental

Since the alkali dissolved from ordinary glass at room temperature is sufficient to change the color of the dilute Congo acid from blue to red it was necessary to carry out all observations in Pyrex or quartz vessels and to use particular care in the purification and storing of all reagents

Preparation of the Blue Sol. A good grade of commercial Congo red was purified by recrystallization from alcohol according to the method of Hunter.⁴ A 5-gram sample of the salt was dissolved in 400 cc of water and a sufficient excess of hydrochloric acid was added to give a blue curd. This curd was thoroughly washed in 250 cc bottles by the aid of the centrifuge, the supernatant liquid after each washing being discarded and replaced by water. At the outset of the washings, a small portion of the blue gel was re-peptized but the bulk of the acid was thrown down during the centrifuging. After several repetitions of the washing process, there came a time when the whole mass of the gel was peptized, none being thrown down by the centrifuge. A sample of this relatively pure, concentrated sol was placed in a Pyrex balloon flask, diluted, and dialyzed in a Neidle dialyzer with a cellophane membrane. After the first day the dialysate gave no test for chlorides but the operation was continued for two weeks in order to get as pure a product as possible. The sol used in the following experiments contained 1.04 gram of the acid per liter.

The Acid from Pyridine. A 2-cubic centimeter sample of the sol was evaporated to dryness on a water bath, in a transparent quartz dish and the residue dissolved in pure pyridine. The deep red solution of the pyridine salt

¹ Kolloidchem. Beihefte, 10, 179 (1919); cf. Schulemann: Biochem. Z., 80, 1 (1917).

² Hantzsch: Ber., 46, 1537 (1913); 48, 158 (1915); Kolloid-Z., 15, 79 (1914); Pihlblad: Z. physik. Chem., 81, 417 (1913); Voigt: Kolloid-Z., 15, 84 (1914); Kruyt and Kolthoff: 21, 22 (1917).

³ Kolloid-Z., 27, 188 (1920); Lüers: 26, 15 (1920).

⁴ Biochem. J., 19, 42 (1925).

was taken to dryness on the water bath. As the evaporation proceeded, and a film of the solid appeared on the wall of the vessel, the crust assumed a reddish-brown appearance. After the liquid evaporated, the deposit was heated in a hot air oven to 120° to remove the pyridine completely. The film was blue by transmitted light and reddish brown by reflected light. Since the surface color of the solid blue acid is reddish brown, it is altogether probable that Schaposchnikoff and Hantzsch who worked with porcelain dishes mistook the brown surface color of the blue acid for the solid red acid.

Solubility of the Blue Acid in Alcohol. Since the blue acid is reported to be fairly soluble in alcohol and acetone it was thought that evaporation of one of these solutions at low temperature might yield the solid red acid. Accordingly, 10 cc of the sol was placed in a 500 cc transparent quartz distilling flask connected to a vacuum pump through a suction flask surrounded by a freezing mixture. Evaporation was hastened by rotating the distilling flask at intervals thus coating the walls with liquid. By this means a film of the acid was deposited which was blue by transmitted light but distinctly reddish brown by reflected light. To the flask was added 50 cc of freshly prepared absolute alcohol. Contrary to what was expected, the acid proved to be almost insoluble giving but a faint brownish-pink solution. Thinking that the evaporation had influenced the rate of solution of the particles, some of the pure sol was added to the absolute alcohol. The addition of 0.05 cc of sol, containing 1 gram per liter, to 10 cc of alcohol gave the brownish-pink color referred to above; 0.1 cc gave a brown; 0.15 cc a lavender; and 0.25 cc a blue. On standing several hours, the excess blue sol coagulated giving the weak brownish-pink solution.

This very slight solubility in alcohol did not agree with the observations reported by others or with our preliminary observations with some stock 95 percent alcohol. With a certain sample of the latter reagent, 3 cc of the sol gave a bright red solution, and 4 cc a brown. This solubility, more than 60 times that in the absolute alcohol, was traced to the presence of alkali dissolved from the soft-glass bottle in which the alcohol was stored for a year or more. A freshly distilled sample possessed the weak solvent action which characterized the absolute alcohol.

The brownish-pink solution in absolute alcohol yields a film of the blue acid on evaporating in a quartz dish. If an extremely dilute pale pink solution is evaporated, the very thin film appears brown rather than blue. It is impossible to say whether this brownish film contains some solid red acid or whether the red present is due to salt formed by interaction with the alcohol or with a minute trace of some impurity therein. The latter seems the more probable in view of the fact that evaporation of a pink aqueous solution gives a film of the blue acid.

Solubility in Water. In some preliminary observations with dilute sols of the blue acid in water, the sol was observed to change from blue to red on heating and to return to blue once more on cooling. In order to study this phenomenon quantitatively, 2 cc of the original sol was diluted to 100 cc with conductivity water. Sols of the concentrations shown in Table I were made

TABLE I
Concentration of Dye Sol used in Experiments recorded in Table II

| Solution No. | Ccs diluted sol in 10 cc | Concentration of dye acid | |
|--------------|--------------------------|---------------------------|----------------------------|
| | | Grams per liter | Milliequivalents per liter |
| 1 | 0.5 | 0.00105 | 0.0032 |
| 2 | 0.75 | 0.00158 | 0.0048 |
| 3 | 1.00 | 0.00210 | 0.0064 |
| 4 | 1.25 | 0.00263 | 0.0080 |
| 5 | 1.50 | 0.00315 | 0.0024 |
| 6 | 1.75 | 0.00368 | 0.0028 |
| 7 | 2.00 | 0.00420 | 0.0032 |
| 8 | 2.50 | 0.00525 | 0.0040 |
| 9 | 3.00 | 0.00630 | 0.0048 |
| 10 | 4.00 | 0.00840 | 0.0064 |
| 11 | 5.00 | 0.01050 | 0.0180 |

up in transparent quartz test tubes that had been thoroughly cleaned. Over the tubes was inverted a short test tube which served to prevent undue evaporation during heating. The tubes were placed in a thermostatically controlled electric oven and heated for 24 hours at each of the temperatures noted in Table II. The level of the liquid in the tubes was marked and the slight loss in water by evaporation was replenished at intervals.

TABLE II
Effect of heating Dilute Sols of the Blue Congo Acid

| Solution No. | Color after heating at | | | | |
|--------------|------------------------|------------------|-----------------|-----------|-----------|
| | 40° | 50° | 60° | 75° | 100° |
| 1 | almost colorless | pink | pink | pink | pink |
| 2 | blue | almost colorless | pink | pink | pink |
| 3 | blue | blue | very light blue | light red | light red |
| 4 | blue | blue | light blue | red | red |
| 5 | blue | blue | blue | lavender | red |
| 6 | blue | blue | blue | lavender | red |
| 7 | blue | blue | blue | blue | red |
| 8 | blue | blue | blue | blue | brown red |
| 9 | blue | blue | blue | blue | brown red |
| 10 | blue | blue | blue | blue | lavender |

The colors of the solutions after heating at the several temperatures are given in Table II. At room temperature all of the solutions appeared blue, differing only in intensity, and remained so indefinitely. On raising the temperature to 40° enough red acid was formed in solution 1 to give a mixture of red and blue that appeared colorless. At 50° most of the blue acid of solution 1 had dissolved, the solution becoming pink or light red. At this temperature, solution 2 became colorless and at 60°, it turned pink. At the same time, red was clearly distinguished in solutions 3, 4, and 5, while at the higher concentration the red was completely masked by the blue. At 100°, the most concentrated solution in the series contained enough red to make it appear distinctly lavender.

If the red solutions are allowed to stand at room temperature they return to the original blue color, the dilute ones passing through the colorless stage. The rate of this change is slower the more dilute the solutions and the freer they are from the blue sol, the presence of which prevents supersaturation. The rate of transformation of a red solution to blue can be hastened by seeding with some of the blue sol.

If this is a case of solution, the amount of red in presence of blue should be the same irrespective of the excess of blue present. Since the solutions are so dilute it was found impossible to determine, by absorption measurements, the amount of red in contact with blue. Moreover, the insoluble blue acid may adsorb some of the red anion thus reducing the concentration of the latter in proportion to the amount of the blue sol present. In spite of this latter source of error, the following observation gives quite conclusive evidence that the color change is the result of a solution process: Solutions numbers 3, 5, and 6 were heated to 70° until 3 became pink with a tinge of blue, 5 light lavender, and 6 lavender. All three solutions were then made the same strength by adding blue sol to solutions 3 and 5 and water to 6. As nearly as could be determined by colorimetric observations all of the sols were now of the same color.

In view of the similarity in color of aqueous solutions of Congo red and of the red acid, it is altogether probable that the color of the latter like the former is due to the red colloidal anion. The blue acid is relatively insoluble but to the extent that it dissolves, it yields a red colloidal anion. From this point of view, the blue color is that of the non-dissociated acid while the red color is that of the ion. Since evidence of the existence of a solid red acid is lacking, it is impossible to say whether there are two structurally different acids of Congo red. It seems unlikely that a change in temperature from 30° to 40° would cause the molecule to change from the azoid to the quinoid structure which Hantzsch assumes; but there is no definite proof either way. In any case, there is no need of assuming such a transformation to account for the observations herein recorded.

Congo Red Lakes

The hydrous oxides of iron, chromium, and aluminum adsorb Congo red forming stable color lakes. From the standpoint of the theory of the lake formation process, the most interesting Congo red lakes are those obtained

from the blue acid. Bayliss¹ found that hydrous alumina adsorbs the blue acid from its colloidal solution. If this adsorption complex is washed, suspended in water, and heated, the color changes from blue to red. Since Congo red salts are red, Bayliss attributed this change in color to the formation of an aluminum salt. The experiments were extended to the precipitates obtained by mixing the blue negative sol with the positive sols of the hydrous oxides of aluminum, zirconium, and thorium. The blue adsorption complex becomes red on heating in every case, provided the hydrous oxide sols are dialyzed until practically free from acid. A small amount of acid is sufficient to prevent the color change. Assuming that the color change is due to the formation of a Congo red salt of aluminum or zirconium, there is no obvious reason why a trace of acid should prevent the change provided there is an excess of hydrous oxide with which the Congo red acid can react.² Blucher and Farnau³ attempted to get around this difficulty by assuming that the hydrous oxide adsorbs and stabilizes the free red Congo acid which they erroneously believed to be instable in aqueous solution.

Wedekind and Rheinboldt⁴ confirmed Bayliss' observation and suggested, but did not prove, that aqueous sols of the blue acid contain more or less red acid which is changed to a blue isomer by acids. The red lake was believed to be a salt of indefinite composition formed by reaction of alumina with the red acid.

Experimental

The Congo red sol used in the subsequent experiments was prepared as previously described. It contained 0.7 grams of the acid per liter. Since alumina gives a typical lake, the alumina sol was used as the starting point in the preparation of all lakes. It was prepared by precipitating a solution of aluminum chloride with ammonia, washing the gel by the aid of the centrifuge, suspending in water and peptizing completely with a small amount of hydrochloric acid. The sol was purified by dialyzing boiling hot in a Neidle dialyzer with a continuous flow of water at the rate of two liters per hour for approximately 100 hours. The sol employed in the following experiments contained 1.7 grams of alumina per liter. Both sols were prepared and stored in Pyrex apparatus and the experiments were carried out in Pyrex tubes steamed before use.

Color of Alumina Lakes. The first series of experiments was carried out to show the connection between the lake color and the relative amounts of dye and alumina. In all cases, the lakes were prepared by the aid of a mixer⁵ which was known to give rapid and uniform mixing of the two constituents. The mixture was poured immediately into Pyrex test tubes which were placed in a water bath at 100° for two hours. Thereafter, the tubes were allowed to

¹ Proc. Roy. Soc., 84 B, 881 (1911).

² Bancroft: J. Phys. Chem., 19, 57 (1915).

³ J. Phys. Chem., 18, 634 (1914).

⁴ Ber., 52, 1013 (1919).

⁵ Weiser and Middleton: J. Phys. Chem., 24, 48 (1920).

TABLE III
Color of Congo Red-Alumina Lakes

| Al ₂ O ₃ | In ccs | Sols mixed (Total volume 25 cc) | | Color after heating | |
|--------------------------------|--------|------------------------------------|-------------------------------------------------------|---------------------|-----------------------|
| | | Dye | In milliequivalents Al ₂ O ₃ | Precipitate | Supernatant liquid |
| 9 | 1 | | 0.9 | Red | Pink |
| 8 | 2 | | 0.8 | Red | Pink |
| 7 | 3 | | 0.7 | Red | Colorless |
| 6 | 4 | | 0.6 | Red | Colorless |
| 5 | 5 | | 0.5 | Purple | Red |
| 4 | 6 | | 0.4 | Purple | Red |
| 3 | 7 | | 0.3 | Purple | Red |
| 2 | 8 | | 0.2 | Blue | Red |
| 1 | 9 | | 0.1 | Blue | Blue |

stand for twelve hours and the observations noted in Table III were made. Although there is present at all times a large excess of alumina, the lakes vary in color from red through purple to blue as the concentration of the dye sol is increased. It will be noted that, as usual, the range of complete mutual precipitation of oppositely charged sols, is narrow.

Effect of Acid. The effect of acid on the color of a given lake is shown in Table IV. It will be seen that under the conditions of the experiment 0.0005 normal hydrochloric acid prevents the formation of a pure red lake. Heating in the presence of acid causes complete coagulation of the sols.

TABLE IV
Effect of Acid on Color of Congo Red-Alumina Lakes

| Ingredients mixed in cubic centimeters (Total volume 25 cc) | | | Color | | | |
|-------------------------------------------------------------------|-----|------------------|-----------------------------------|------------|---------------|-----------|
| Al ₂ O ₃ | Dye | HCl (0.025 N) | Without heating after two days | | After heating | |
| | | | Precipitate | Liquid | Precipitate | Liquid |
| 5 | 2 | 0.0 | Red | Colorless | Red | Colorless |
| 5 | 2 | 0.5 | Blue | Red | Purple | Colorless |
| 5 | 2 | 1.0 | Blue | Pale blue | Purple | Colorless |
| 5 | 2 | 2.0 | Blue | Light blue | Purple | Colorless |
| 5 | 2 | 4.0 | {No Precipitate | Blue | Purple | Colorless |
| 5 | 2 | 6.0 | | Blue | Blue | Colorless |

Mechanism of the Lake Formation Process. In the light of the above observations and those recorded in the previous section, the mechanism of the formation of the lakes appears to be as follows: In the blue sol the following equilibria are set up:



where R'' is the anion of Congo red. Rise in temperature displaces the equilibria to the right. On mixing the hydrous oxide sol with the blue dye, mutual coagulation of oppositely charged particles results in the formation of a blue lake. Following this process the alumina adsorbs the red colloidal ion shifting the equilibrium gradually to the right. The color of the lake ultimately formed depends on the hydrogen ion concentration and the amount of the blue dye. If the amount of dye is not in excess of the adsorption capacity of alumina for the red anion, the lake will be red. If there is an excess of the blue dye, the blue color blends with the red giving purple or if the excess of blue is sufficiently great the red color is masked completely. Rise in temperature increases the rate at which the adsorption equilibrium is set up. The addition of even a small amount of acid cuts down still further the low solubility of the acid as well as the degree of ionization of the acid, and blue lakes only are formed.

From these considerations it follows that if the excess of blue dye above the adsorption capacity of alumina for the red anion, were such that it would dissolve and become red on heating, the lake should be red when hot and purple to blue when cold. This proved to be the case: To 25 cc of a blue sol containing 0.00067 gram of dye was added 1 cc of the alumina sol. The blue lake was changed to red on heating but on standing for some time at room temperature, it became purplish blue.

The observations indicate that the red lake like the blue is an adsorption complex and not an aluminum salt. If the alumina sol is free from cations other than hydrogen, then the red lake consists ultimately of an adsorption complex of alumina and the red acid. To the extent that alkali or ammonium cations are present, the dye may be held as the red alkali or ammonium salt. Bancroft¹ believes that some ammonium must be present in the alumina and chromic oxide sols used by Weiser and Porter² in preparing their alizarin lakes, otherwise the lakes would not be red, since alizarin is yellow and not red. This contention is valid unless it should turn out that a thin film of alizarin adsorbed on a hydrous oxide is red.

The mechanism of the dyeing of cotton red from the sol of the blue acid is similar to that of the formation of the red color lakes.

Summary

1. Aqueous solutions of Congo red contain a red colloidal anion which is too small and hydrous to be visible in the ultramicroscope but which will not pass a membrane permeable to ions in true solution.
2. Replacing the sodium in Congo red with hydrogen gives a blue colloidal acid. A typical equation for the reaction is: $2 Na' + R'' (\text{red}) + 2 H' + 2 Cl' \rightleftharpoons H_2R (\text{blue}) + 2 Na' + 2 Cl'$, where R'' stands for the anion of the dye. Since this reaction is partly reversible Congo red is not suitable for an indicator in acidimetry, in the presence of salts.

¹ Private communication.

² J. Phys. Chem., 31, 1824 (1927).

3. The blue acid is very slightly soluble in water yielding the red colloidal anion. The solubility increases with rising temperature. In the blue sol the following equilibria exist: nH_2R (blue) \rightleftharpoons nH_2R (in solution) \rightleftharpoons $2nH^+ + nR''$ (red).

4. The positively charged hydrous oxide mordants, such as alumina, adsorb the blue colloidal acid giving blue lakes. If the amount of blue acid is small the blue lakes change to red very slowly at ordinary temperatures and more rapidly at higher temperatures. The process consists in the adsorption of the red anion by the hydrous oxide displacing the reaction given in (3) to the right until all the blue acid disappears. If the hydrogen ion concentration of the bath is too high or the amount of blue acid is in excess of the adsorption capacity of the hydrous oxide for the red anion, the lake remains purple to blue in color.

5. The blue lake is an adsorption complex of the blue acid and the hydrous oxide. The red lake is an adsorption complex of hydrous oxide and the red acid (or alkali salt). The red alumina lake is not an aluminum salt of Congo red as assumed by Bayliss.

6. The mechanism of the dyeing of cotton red from a sol of the blue acid is similar to that of the formation of the red hydrous oxide lakes.

7. Definite assurance of the existence of the red Congo acid in the solid state is lacking. The product formed by decomposing the pyridine salt is blue by transmitted light and reddish brown by reflected light. It is probable that Schaposchnikoff and Hantzsch mistook the surface color of the blue acid for the alleged red isomer.

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SOME EXPERIMENTS ON THE PRODUCTION OF COLOR IN GLASS AND IN GEMS BY X-RAYS AND RADIUM RAYS

BY M. C. REINHARD AND B. F. SCHREINER*

It is well known that intense X-radiation causes glass to take on color depending on its chemical composition. Lead glass is colored brown and glass containing manganese is colored purple. Recently we have exposed to X-rays samples of a special glass containing various amounts of bismuth.¹ After twelve hours of exposure this glass became yellow in color. The depth of color produced did not in any way parallel the concentration of bismuth.

This coloration in the glass is fairly permanent, requiring heating almost to the melting point in order to restore the original color. On the other hand, Bayley² has found that some inorganic crystals when colored by X-rays lose their color as a result of exposure to ordinary white light.

In view of these results and since glass which is a silicate takes on color as a result of radiation it seemed reasonable to expect that certain gems, some of which also are silicates, might be changed in color by similar radiation. The following gems were therefore exposed to the β and γ radiation from radium and also to X-rays. The gems were:

| | |
|--------------------|------------------------------------------|
| Topaz | $\text{Al}_2\text{F}_2\text{SiO}_4$ |
| Aquamarine | $\text{Be}_3\text{Al}_2(\text{SiO}_3)_2$ |
| Amethyst | SiO_2 |
| White diamond | |
| Garnet | $\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$ |
| Brown diamond | |
| Imitation emerald. | |

These gems were placed next to a glass bulb containing one gram of radium in solution as radium bromide and 15 cm away from another bulb also containing one gram of radium in solution (the radon was removed daily from over these two solutions.) The gems were left in this position for twenty days. The radiation is not as intense as at first apparent because the radon is expanded in a considerable volume and it is removed daily. In spite of this the gems must have received considerable β and γ radiation. They showed however, no color change.

The stones were therefore, placed at a distance of 70 cm. from the target of an X-ray bulb which was operated at 200,000 volts and 30 milliamperes for 100 hours of intermittent radiation. The radiation was unfiltered. This

*From the State Institute for the Study of Malignant Disease, Buffalo, New York, Burton T. Simpson, M.D., Director.

¹ Supplied by Professor E. R. Riegel, University of Buffalo.

² P. L. Bayley: Phys. Rev., (2) 24, 495 (1924).

intensive exposure also failed to produce a noticeable change in the color of any of the gems. Very much less time of exposure would have produced color in glass.

The brown and the white diamond were next placed immediately beneath a glass bulb, 3 mm in diameter, containing 440 millicuries of radon. The diamonds would with this arrangement receive both the β and γ radiation from the radon. The white diamond immediately fluoresced in a beautiful blue color whereas no fluorescence at all could be observed in the brown diamond. Coolidge and Moore¹ report that with high-voltage cathode radiation they obtained blue fluorescence in 22 out of 24 diamonds, one of the remaining showed yellow and the other green fluorescence.

The diamonds were left beneath the radon bulb for a total of 60,700 millicurie hours. No color change could be detected when the radon was removed. This is in accord with Lind and Bardwell² who conclude that diamond is not colored by β and γ rays from radium in a glass container 0.5 to 1 mm. thick.

None of the other gems showed any fluorescence when exposed to the rays from a glass bulb containing 150 millicuries of radon.

Natural quartz crystals were also exposed to intense X-radiation but showed no color change after 35 hours of exposure. Fused quartz, on the other hand, became brown in spots, other areas remaining clear. This same effect was produced by Coolidge³ with cathode rays from his new high-voltage cathode ray tube.

Summary

The following gems are unaffected by very intense X-radiation and by β and γ rays from radon: topaz, aquamarine, amethyst, garnet, white diamond, and brown diamond.

The white diamond fluoresced in a beautiful blue color when exposed to a radon tube; none of the other gems fluoresced.

Natural quartz is unchanged, while fused quartz is colored in an irregular brown pattern by X-rays.

¹ Coolidge and Moore: J. Franklin Inst., 202, 727 (1926).

² Lind and Bardwell: J. Franklin Inst., 196, 52 (1923).

³ Coolidge and Moore: J. Franklin Inst., 202, 722 (1926).

THE CONSTANT-BOILING MIXTURE OF HYDROGEN FLUORIDE AND WATER

C. W. MUEHLBERGER

In 1843, Bineau¹ pointed out that the hydrohalogen acids formed constant-boiling mixtures and attempted to identify these azeotropic mixtures as definite hydrates of the acids. He showed that under ordinary atmospheric conditions, aqueous hydrofluoric acid of 35.6 to 37.6% concentration distilled at constant composition. He reported that the constant-boiling mixture boiled at 120° and had a density of 1.15. Roscoe² later studied the constant boiling mixtures of aqueous solutions of the hydrohalogens and, in addition to confirming Bineau's experimental work, he showed that the composition of the equilibrium mixture was a function of the temperature at which the equilibrium was reached. Thus, at the ordinary boiling point of aqueous hydrofluoric acid under a pressure of one atmosphere, the equilibrium mixture was found to be 36 to 38% hydrogen fluoride. However, at 15°, the equilibrium mixture was 32.5%. By this type of experimentation, Roscoe showed the fallacy of Bineau's hypothesis of the formation of definite hydrates.

More recent work by Deussen³ showed that at atmospheric pressure the constant boiling mixture of aqueous hydrofluoric acid was 43.2% hydrogen fluoride. This mixture was said to have a density of 1.138 at 18° and a boiling point of 111° at a pressure of 750 mm. of mercury. For these experiments he used a platinum still fitted with a thermometer well. The concentration of his solutions was determined by titration with barium hydroxide solution which had previously been standardized with crystallized potassium hydrogen fluoride, using phenolphthalein indicator.

In our laboratory, distillations of pure aqueous hydrogen fluoride made in a platinum apparatus have indicated that the constant-boiling mixture is 38.18% HF ($\pm 0.10\%$) at a pressure of 735 mm. of mercury. The density of this concentration of acid, as determined with a Westphal balance fitted with a Bakelite plummet, was found to be 1.138 at 20°. This agrees with the density reported by Deussen but is considerably higher than the density of 38.18% hydrogen fluoride given by Winteler⁴. The boiling point of the azeotropic mixture was determined in a lead distilling apparatus fitted with a thermometer well and was found to be 110.8° at a pressure of 732 mm. of mercury.

The concentration of the constant-boiling acid was determined by titration with 1.5 normal sodium hydroxide solution using phenolphthalein as an indicator. Precautions were taken to exclude carbonates and silica from the reagents and to insure that the hydrofluoric acid used was free from impurities.

¹ Ann. Chim. Phys., (3) 7, 257-75 (1843).

² Ann., 116, 203-220 (1860).

³ Z. anorg. Chem., 49, 297-300 (1906).

⁴ Winteler: Z. angew. Chem., 1902, 33-34.

Constant boiling hydrochloric acid¹ and carefully crystallized oxalic acid² were used as primary standards in determining the concentration of the standard alkali solution.

From these results it is apparent that the concentration of the constant-boiling mixture of aqueous hydrofluoric acid reported by Deussen is too high. This error may have been due to impurities in the KHF₂ which he used as an acidimetric standard.

The writer is greatly indebted to Prof. George Kemmerer and other members of the Chemistry Faculty of the University of Wisconsin for their kindness in providing apparatus and other facilities, without which this work would have been impossible.

*University of Wisconsin,
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April 25, 1928.*

¹ Foulk and Hollingsworth: *J. Am. Chem. Soc.*, 45, 1227 (1923).

² Hill and Smith: *J. Am. Chem. Soc.*, 44, 546-557 (1922).

NEW BOOKS

Photochemical Processes. By George B. Kistiakowsky. 28 × 16 cm; pp. 270. New York: Chemical Catalog Company, 1938. Price: \$5.50. The subject is treated under the general headings: the concept of light quanta and photochemical kinetics; the equivalence law; chain reactions; photosensitisation; catalysis and inhibition; frequency of radiation, temperature, and the rate of photochemical reactions.

In the foreword Professor Taylor says, p. 7: "The present volume has attempted an analysis, from the stand-point of quantum theory, of those photochemical reactions of which the study has been sufficiently detailed so that some definite conclusions concerning the kinetics of the process can be reached. . . . *The absorption of light is a quantum process involving one quantum per absorbing molecule (or atom). The photochemical yield is determined by the thermal reactions of the system produced by the light absorption.* The following pages will show, I believe, that such a generalisation is adequate to the facts now known."

The reviewer is not yet convinced of this. He has not found any real attempt to prove the truth of the fundamental hypothesis that the first stage in a photochemical process is the absorption of exactly one quantum of light. The reasoning seems to him to be something like this. If we assume that the first stage is the absorption of exactly one quantum, higher yields must be due to a chain reaction. We find higher yields in many cases and we are therefore dealing with chain reactions in these cases. Of course it is not put quite so baldly as this. On p. 123 another criterion is suggested, though very little use is made of it and no attempt is made to prove that it can only occur with chain reactions.

"Besides acetone hydrolysis, such reactions as the decomposition of ozone in ultra-violet and visible light, the decomposition of hydrogen peroxide, the oxidations of hydriodic acid, of sulfites, of iodoform, and several others, must be enumerated among chain reactions. Besides an excessive quantum yield observed in many of these reactions, they possess another property common to chain reactions. We have repeatedly observed that those reactions which have an exceedingly large quantum yield are particularly sensitive to the presence of even small traces of foreign substances, the presence of which either accelerates or retards the rates of these reactions."

One wonders to what extent adsorption plays a part in photosensitisation by zinc oxide, p. 155. "A large variety of photosensitised reactions has been shown in recent years to be due to the action of solid particles of zinc oxide. Eibner demonstrated that oil paints containing zinc oxide are destroyed more rapidly by light than those containing other inorganic substances. Winther studied the fluorescence of zinc oxide and some of its photosensitising actions. For both processes, the near ultraviolet spectral region was found to be effective. Winther demonstrated that, in presence of illuminated zinc oxide, glycerin is oxidised to glycerose and that this process can be carried out either in presence of free oxygen or in presence of different inorganic compounds. In absence of air, lead carbonate is, for instance, reduced to metallic lead by the reducing action of glycerin. Winther suggested that the zinc oxide remains chemically unchanged during these reactions and supported his view by experiments which showed that actually the size and shape of single zinc oxide particles remain unchanged even on prolonged illumination in presence of glycerin and lead carbonate." It looks as though it were not good form for the catalytic hand to let the photochemical one know what the former is doing.

There is an interesting passage on p. 237. "The existence of light-absorbing centres in a single molecule suggests, further, the possibility of several distinct photochemical processes caused in the same light-absorbing molecule by light of different frequencies. This problem is undoubtedly of considerable interest, but unfortunately very little experimental work has been done in this direction."

The author apparently accepts, p. 196, the view of Moureu and Dufraisse that "normally oxidations by free oxygen proceed through an intermediary formation of an instable per-

oxide and that inhibitors act by destroying this peroxide." "The chain character of the photochemical oxidation of sodium sulfite was demonstrated by Bäckström, since he found as many as 50000 molecules per absorbed quantum of wave-length 2536Å."

Whether one agrees with the main thesis of the author or not—and the reviewer does not—we are indebted to him for the admirable way in which he has presented the enormous mass of data. The subject matter is well arranged and the view-point is held to consistently.

Wilder D. Bancroft

Biochemical Laboratory Methods for Students of the Biological Sciences. *By Clarence A. Morrow.* 23 × 15 cm; pp. xvii + 350. New York: John Wiley and Sons, 1927. Price: \$3.75. The reviewer must first express most sincere regret at the death of the author which occurred prior to the publication of this excellent book. It is a manual for use in training students in the laboratory methods of biological chemistry with emphasis somewhat upon the plant side, and is the outgrowth of nine years' experience in biochemical laboratory methods. Two hundred thirty-three experiments are described.

There are nine chapters: the colloidal state; physical chemical constants of plant saps; hydrogen-ion concentration and buffer action; proteins; carbohydrates; glucosides; fats and allied substances; enzymes; plant pigments.

A list of well-chosen references at the end of each experiment is an admirable feature as in the introduction of sufficient theoretical material in the experimental descriptions to clearly point out the connection between the two.

The book is designed for students with a previous knowledge of quantitative analysis and organic chemistry with a view to training in research methods. The question arises whether such a book might not better be designed to follow also an introductory course in physical chemistry.

Robert L. Nugent

Das periodische System in neuer Anordnung. *By Darwin O. Lyon.* 18 × 26 cm. Leipzig and Vienna: Frank Deuticke, 1928. Price: 8 marks. Dr. Lyon has written in English, and published in German, a Thesis on the Periodic Classification of the Elements. The introduction deals with insoluble problems, such as the relative abundance of the chemical elements in nebulae, in stars and in the interior of the earth, and the processes of transformation involved in their synthesis and decay; but the principal contents of the pamphlet are a series of tables and spirals in which the periodic system is presented in a modified form, as it has been by many other authors. The principal justification for issuing the pamphlet may be found in two tables and a series of diagrams in which 15 of the physical properties of the elements are set out (1) in order of atomic numbers, (2) in order of magnitude. These will give an opportunity to the earnest student to explore more fully the implications of the Periodic Law, but the only important novelty appears to be the grouping of paramagnetic and diamagnetic elements in clusters of 3 + 5 in the short periods and of 3 + 4 + 3 and 3 + 5 in the long periods of Mendeléeef's classification. The element of research is represented by a study of tables of data rather than by experimental work.

T. M. Lowry.

Über Lösungs- und Verdünnungswärmen einiger starker Elektrolyte. (*Fortschritte der Chemie, Physik und physikalischen Chemie, Band 19, Heft 6*). *By Erich Lange.* 25 × 17 cm; pp. 83. Berlin: Gebrüder Borntraeger, 1928. Price: 6.40 marks. The importance of the heats of solution and dilution of strong electrolytes in connection with the theory of complete ionisation is obvious, and the present monograph serves a useful purpose in bringing together a brief account of the theoretical side of the subject and the rather scanty experimental results, for aqueous solutions only. The literature references are complete, include American publications, and are brought up to the date 1927. Brief accounts of the experimental methods are included. The interesting connection between heat of solution and the lattice energy of salts is considered.

J. R. Partington

American Lubricants. By L. B. Lockhart. Third edition. 23 × 16 cm; pp. xi + 408. Easton: The Chemical Publishing Company, 1927. Price: \$5.00. The second edition was reviewed more than seven years ago (25, 427). In bringing the new edition up to date the size of the book has been increased about twenty percent. The book is written "to aid the user and the buyer of lubricants in a more intelligent selection of oils and greases. The point of view throughout is that of the user rather than that of the refiner."

Wilder D. Bancroft

Errata

In the paper by D. H. Peacock (31, 535), the name of S. C. J. Olivier should be substituted for that of Holleman in connection with the second foot-note on p. 535. On p. 540 the first equation should be changed to read:

$$k = N\sigma^2 \sqrt{8\pi RT(1/M_A - 1/M_B)} \cdot e^{-(Q_A + Q_B)/RT}$$

In the paper by Andrews and deBeer (32, 1031), change the $-Y$ above (3) on p. 1031 to $+Y$. On p. 1033 nineteen lines from the top, change 100 cc to 300 cc. On p. 1035 under C, change -0.11° to $+0.11^\circ$. On p. 1038 change 1.20° to 12.0° .

In the paper by F. F. Sherwood and E. I. Fulmer (30, 738) the first equation in Table IX on p. 745 should read $0.0960 + 0.0306t$. For Table XVI on p. 752, substitute the revised table given below.

VALUES OF k , Q_{10} , and μ FOR THE GROWTH OF YEAST IN VARIOUS MEDIA

| t° | W ₀ | | | W ₁ | | | E ₀ | | | E ₁ | | | Slator | | |
|----|---------------------|-----------------|-----------------|---------------------|-----------------|-----------------|---------------------|-----------------|-----------------|---------------------|-----------------|-----------------|-----------------|-----------------|--|
| | k × 10 ² | Q ₁₀ | μ ₁₀ | k × 10 ² | Q ₁₀ | μ ₁₀ | k × 10 ² | Q ₁₀ | μ ₁₀ | k × 10 ² | Q ₁₀ | μ ₁₀ | Q ₁₀ | μ ₁₀ | |
| 0 | 1.22 | | | 4.53 | | | | | | 1.13 | | | | | |
| 5 | (2.6) | | | (7.4) | | | | | | (2.55) | | | | | |
| 10 | 4.30 | 3.52 | 19430 | 10.92 | 2.39 | 12800 | 3.24 | | | 4.05 | 3.52 | 19430 | 5.62 | 6580 | |
| 15 | (7.1) | | 16060 | (14.0) | | 10200 | (5.2) | | | (6.20) | | 16470 | 3.82 | 1350 | |
| 20 | 10.35 | 2.41 | 14150 | 17.80 | 1.63 | 8087 | 7.77 | 2.40 | 14500 | 8.83 | 2.18 | 12580 | 2.81 | 7060 | |
| 25 | (13.5) | | 11000 | (19.4) | | 5606 | (10.4) | | 11890 | (11.20) | | 10080 | 2.21 | 3520 | |
| 30 | 16.6 | 1.63 | 9210 | 20.51 | 1.15 | 2531 | 13.61 | 1.75 | 9922 | 13.61 | 1.54 | 7650 | 1.91 | 1390 | |
| 35 | (19.0) | | 6241 | (20.4) | | 988 | (13.4) | | 4645 | (14.2) | | 4808 | 1.6 | 8618 | |
| 40 | 19.36 | 1.15 | 2617 | 20.05 | 0.97 | -1403 | 13.16 | 0.966 | -1403 | 14.52 | 1.07 | 1281 | | | |
| 42 | 19.23 | 0.99 | -2343 | | | | 10.98 | 0.834 | | 12.39 | 0.85 | | | | |
| 43 | 1.80 | 0.093 | | | | | | | | 1.43 | 0.115 | | | | |

W₀ = wort with no ammonium chloride

W₁ = wort with optimum concentration for each temperature.

E₀ = Medium E kept optimum for 30°.

E₁ = Medium E optimum for each temperature.

(Slator (1903)).





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